Adaptive techniques for ultrafast laser material processing

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HABILITATION A DIRIGER DES RECHERCHES

PRESENTEE DEVANT

L'UNIVERSITE JEAN MONNET

par
Razvan Stoian

JURY

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A very special chapter is dedicated to my wife, Diana. Every time I looked over my shoulder, she was there, standing by me right from the beginning. It is hard to imagine having made it to this point without her.

Abstract

Requirements for high accuracy in laser material processing triggered a considerable amount of effort in investigating ultrashort pulse laser effects in structuring materials on micro and nanoscales. Minimal energy diffusion and high nonlinearity of interaction indicate the possibility of confining energy on smallest spatial scales. The potential of inducing fast structural transitions and generating novel material states with upgraded properties and functions makes ultrashort pulses instruments of choice for precision transformation and structuring of materials. The analyses of ablation phases, material transformation mechanisms, and, especially, their characteristic dynamics offer in turn the key to optimizing laser-matter interaction in view of various criteria related to laser processing: efficiency, accuracy, quality. This thesis summarizes previous works of the author on investigating static and dynamic effects of ultrafast laser energy deposition, with application in material processing. The knowledge derived from the dynamic material response indicates energy relaxation times as a guideline for synergetically improving the interaction between radiation and matter. This is achieved by adapting the incoming energy rate to the material reaction time using newly developed techniques of spatio-temporal beam forming. Optimal coupling of energy gives the possibility to guide the material response towards user-designed directions, offering extended flexibility for quality material processing, and, perhaps, the necessary insight into developing “smart” processing technologies.

Resume

Le besoin d'une très grande précision lors du traitement des matériaux par laser a fortement encouragé le développement des études de l'effet des impulsions ultra brèves pour la structuration des matériaux à une échelle micro et nano métrique. Une diffusion d'énergie minimale et une forte non linéarité de l'interaction permet un important confinement énergétique à des échelles les plus petites possibles. La possibilité d'introduire des changements de phases rapides et même de créer de nouveaux états de matière ayant des propriétés optimisées et des fonctions améliorées donne aux impulsions ultra brèves de sérieux arguments pour être utilisées dans des dispositifs très précis de transformation et de structuration des matériaux. L'étude de ces mécanismes de structuration et, en particulier, de leurs caractéristiques dynamiques, est une clé pour l'optimisation de l'interaction laser-matière suivant de nombreux critères utiles pour les procédés laser : efficacité, précision, qualité. Ce mémoire synthétise les travaux de l'auteur sur l'étude statique et dynamique du dépôt d'énergie ultra rapide, avec application aux procédés laser. La connaissance de la réponse dynamique des matériaux après irradiation laser ultra brève montre que les temps de relaxation pilotent l'interaction lumière-matière. Il est alors possible d'adapter l'énergie déposée à la réponse du matériau en utilisant les toutes récentes techniques de mise en forme spatio temporelle de faisceaux. Un couplage optimal de l'énergie donne la possibilité d'orienter la réponse du matériau vers un résultat recherché, offrant une grande flexibilité de contrôle des procédés et, sans doute, la première étape du développement de procédés « intelligents ».

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Introduction

Right from the beginning of the research carrier, my activity could be positioned into the frame of laser-matter interactions. The present work follows the progress in investigating laser-induced effects with emphasis on material-processing issues. The general scientific outline of these studies was determined by the observation of two main development tendencies in laser material processing, namely:

- an intense effort in micro and nano-technologies and material structuring as the main advance factor for new application areas in emerging technologies,
- the requirement of reliable 2D/3D processing techniques where ultrafast laser-based technology holds benefits for the development of precise processing tools that can structure materials with high degree of accuracy and reduced residual damage.

In this context of increasing demand for precise microfabrication, ultrafast laser modification of materials opens new perspectives for upcoming applications. Material characteristics can be designed on minimal scales, carrying new mechanical, electrical, and optical properties. Due to low thermal character and highly nonlinear interaction, ultrafast laser technology has come forward as a feasible method to design local properties by structuring materials of interest in two and three dimensions. The drive is to achieve control and to design mesoscopic material modifications, thus adding new features and functions to the structured matter.

The field of laser-material interactions is inherently multidisciplinary. Upon impact of a laser beam on a material, electromagnetic energy is first converted into electronic excitation. Then, by specific electron-lattice interactions, the energy is transferred to the heavy particle matrix, being transformed into thermal, chemical, and mechanical forms. During the whole process, the molecular structure and the macroscopic properties of the material are changed in various ways, culminating with permanent alterations, optical damage, and ablation. In the case of ultrashort laser pulses, advantages are to be found in nonlinear, non-thermally induced phase transitions, and in minimally-diffusive energy input, enhancing the overall precision and controllability of the interaction process. In the presence of non-equilibrium phenomena, exotic thermodynamic paths can be induced, rendering accessible states around the critical point. Nevertheless, the result of the laser action depends on the nature of the material. The balance of electronic and structural transformations defines the result of the laser action. Therefore, mastering the induced modifications requires extensive knowledge on the nature of

light-induced matter transformation. Benefits are seen for superior material processing techniques. From here, a strong interest has been derived for studying the mechanisms of laser ablation, including the possibility to control material reactions and modifications.

A large effort to develop laser processing techniques takes place world-wide, fueled by the potential of ultrafast laser radiation to confine energy on mesoscopic scales. Leading laser fabrication and developing centers were established, notably in Germany, Japan, United States, and Canada, and some of the research highlights will be discussed along this work. This concentrated effort succeeded to reach a considerably high accuracy and ablation efficiency, stimulating industrial insertion in the manufacturing and photonic industry. The effort is focused on two main research and development axes: optimizing the process for increased performances and designing laser sources feasible for structuring procedures. The technical implementation of novel technologies is related to the possibility of demonstrating new and even higher levels of controllability, responding to the most stringent demands concerning processing precision and quality. My research activity frames part of these efforts of developing ultrafast laser processing technologies by proposing new solutions to present limitations, as well as by setting up a scientific and technological platform dedicated to material processing and engineering.

The research activities that will be described in the following sections are the sum-up of more than 10 years of expertise in the field of laser processing in various public research establishments located in several countries. This work summarizes activities performed at the Max-Born Institute in Berlin (MBI) during my doctoral stage as well as in the postdoc years that followed. It continues with a description of my current research involvement at the Laboratoire Hubert Curien in Saint Etienne (LabHC) as a CNRS researcher, and, additionally, of the results obtained in the frames of various theses I have coordinated or supervised. In short, after a brief intermezzo in pulsed laser deposition techniques and laser-induced ultrasounds at the Institute of Atomic Physics in Bucharest, the research activity has focused on programs dedicated to ultrashort pulsed laser ablation and laser-induced modification of matter. My scientific pursuit concentrated on investigating fundamental aspects of laser-matter interaction and, subsequently, on further developing laser technologies for structuring and functionalization of materials. This was also integrated in a large partnership with the activity of other colleagues, having the main goal to determine possible applications in emerging add-on technologies such as in photonics, sensorics, tribology, etc. Methods based on optical, electron and ion/neutral mass spectroscopy, ex-situ analyses of surfaces by means of optical, electron, and atomic force microscopy were developed to probe laser-induced

phenomena, including incubation effects, electrostatic disruption of dielectric surfaces, or time-resolved dynamics of the ablation processes. A particular interest was put in analyzing essential factors leading to different ablation phases. The kinetic properties of various types of material ejecta were analyzed and, based on mechanistic and thermodynamic arguments, the possibility of electrostatic ejection of ions from charged dielectric surfaces was indicated. The dynamics of energy relaxation and particle ejection was also investigated for metals and semiconductors, emphasizing the strong thermal component in the ablation products. Optical and spectroscopic methods were developed and applied to interrogate the evolution of matter. At the same time, the material reaction was analyzed theoretically using drift-diffusion approaches or hydrodynamic codes encompassing electronic effects and realistic equation of states. The observation procedures were extrapolated to bulk transparent materials, summing up investigating efforts on nonlinear pulse propagation, thermo-mechanical evolution, and laser-induced refractive index changes. Experimental approaches based on advanced microscopy techniques were combined with numerical simulation tools, which allowed us to follow in space and time pulse propagation effects, nonlinear energy deposition, as well as the subsequent thermo-elasto-plastic material response.

The degree of precision is determinant for many end-user applications and one pertinent question is how to improve the present situation. Moreover, there is potential in achieving material transformations that are not easily accessible by triggering new ways of non-thermal, non-equilibrium evolutions. How to achieve these states? To which extent are laser-induced transitions controllable and how can we design the final state? These are some of the questions my work has tried to deliver, I hope, a pertinent answer. Therefore, apart from the comprehension effort related to laser-excitation mechanisms, a new objective was developed; namely to design structural modifications with predictable properties by taking advantage of adaptive irradiation systems and self-optimization loops. The original idea was determined by previous successful efforts in other science and technology fields, particularly in femtochemistry, to apply a new approach, i. e. the concept of optimal control involving the intelligent assistance of light, in determining specific reaction evolution. Initially used to control energy localization and particular molecular bond disintegration following user-designed chemical paths, this type of approach was integrated in a broader view of controlling complex systems using laser radiation. These previous efforts and the recent development of efficient light-modulating devices allowed us to believe that a processing technique may be developed that is flexible and adaptable, responding “intelligently” to material reaction and taking advantage of changes in materials during irradiation. To achieve this objective, a

material structuring approach based on adaptive pulse spatio-temporal manipulation for optimizing ultrafast laser-induced processes was developed. This requires real-time pulse control and challenges were taken in precisely evaluating and quantifying the laser action for the establishment of self-learning feedback loops. New functional degrees of freedom are in principle possible by adjusting the energy flow to the material properties. The technique, which exploits the laser pulse coherence, facilitates energy transfer and control on structural and thermodynamic phase transitions, allowing extended degree of flexibility in manipulating matter properties. As the characteristics are defined by the type and the scale of the modification, and the technique offers at the same time beam manipulation capabilities in temporal and spatial domains, it puts forward two perspectives for material modification:

- *the engineering aspect*, using the potential of designing irradiation geometries by spatial tailoring of excitation in arbitrary patterns or corrective procedures for distortions inherent to optical beam propagation,
- *the phenomenological aspect*, related to controlling laser-induced physical phenomena by temporal synchronization between radiation and the material reaction, and, eventually, guiding the material response away from the standard relaxation, towards a user-defined behavior.

This approach is aimed to correlate irradiation conditions and material properties in a synergetic manner for optimal laser processing applications. The radiation will adjust to the material in such a way that the material properties themselves will start to play a role in the structuring process. Thus, nonlinear and selective, non-thermally or thermally driven interactions may be determined by spatio-temporal beam engineering with new opportunities for optimal processing. Ultrafast laser-driven phase transition or exotic metastable states are some of the observations that point towards novel properties and the potential of obtaining singular laser machining technologies suitable for a broad range of applications. These techniques are conceived to generate new matter properties and phases based on synergies with material intrinsic reactions, thereby unfolding new perspectives for “smart”, feedback assisted processing of materials. In all these cases the solution is achieved without prior knowledge of the physical aspects of the problem, but the optimal sequences retains the mechanisms of control.

From a time perspective, the timescale of adjustment (sub-picoseconds to picoseconds) allows to control the excitation processes and the follow-up relaxation. To this purpose we have also designed time-resolved techniques for these particular timescales. Insights are delivered concerning the physical aspects and the control factors for laser

interactions, enlarging thus the knowledge basis. This additionally implies prospecting the advantages in the technological implementation of "smart" matter- and shape-adaptable processing machines.

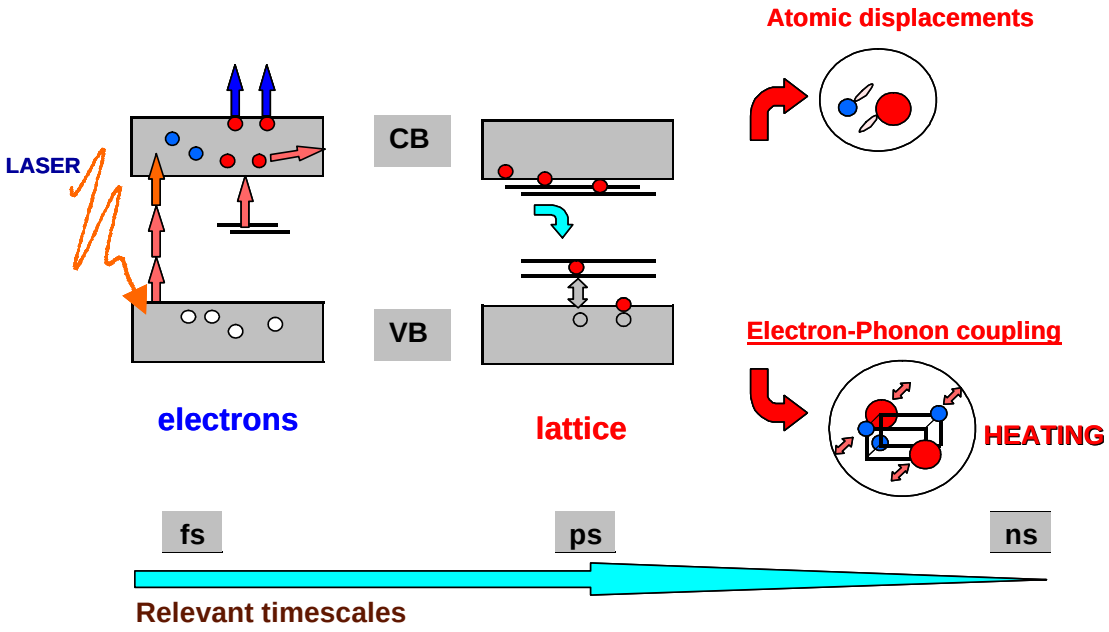

Figure Introduction 1: Potential physical phenomena induced during ultrafast laser excitation of materials, emphasizing the control factors for energy coupling (nonlinear absorption, optical breakdown, photoemission, phonon-generation, local atomic displacements, heating, non-equilibrium thermodynamic phenomena).

The research directions followed up to date involve multidisciplinary approaches based on laser development, advanced observation systems, material science and engineering, with several proposed objectives:

- To explore possibilities and limitations of ultrafast laser-based technology,
- To evaluate the potential of "intelligent" adaptive control in material processing,
- To propose integrated laser methodologies for micro/nano fabrication,

with the purpose to advance laser micro and nanofabrication techniques.

In this frame, my research activity focused on several aspects which are intrinsically related, and a complex methodology was consequently developed in the recent years. Several research directions were advanced, concentrating on the problematic given by the dual aspect of interaction, basic and technological investigations:

- studying laser ablation mechanisms and the material response to laser radiation,
- developing adaptive laser technologies based on spatio-temporal pulse tailoring,
- controlled phase transitions at non-transparent interfaces.
- controlled refractive index changes in optical materials for optical functionalization,

The challenge is to generate user-designed modifications in a self-improving way, bypassing thus the limitation of the standard laser processing techniques and reaching superior controllability. Adaptive self-improving techniques may circumvent the limitation associated with the complexity of irradiation and compensate the a priori lack of information by offering extended flexibility. This additional controllability is a desired factor when approaching the multidisciplinarity of laser-matter interactions. A schematic view of the complex nature of the various physical aspects involved in the laser energy coupling with the typical scales of energy relaxation is illustrated, serving as a guideline for implementing pulse tailoring procedures.

Following this trend, the research activity has tried to answer the following points:

- to trace the laser energy transfer on ultrafast time scales from the initial interaction with the electronic system to the delayed deposition into the lattice and subsequent material removal,
- to identify processes determined by the local deposition of energy, emphasizing the dynamics and the particular temporal scales of the processes involved, while evaluating the possibility to control and regulate the respective mechanisms.
- to prospect the use of temporally shaped pulses to increase the efficiency and the quality of material modification in the μm and sub-μm range - for material removal from the surface as well as for refractive index modifications in bulk optical materials.

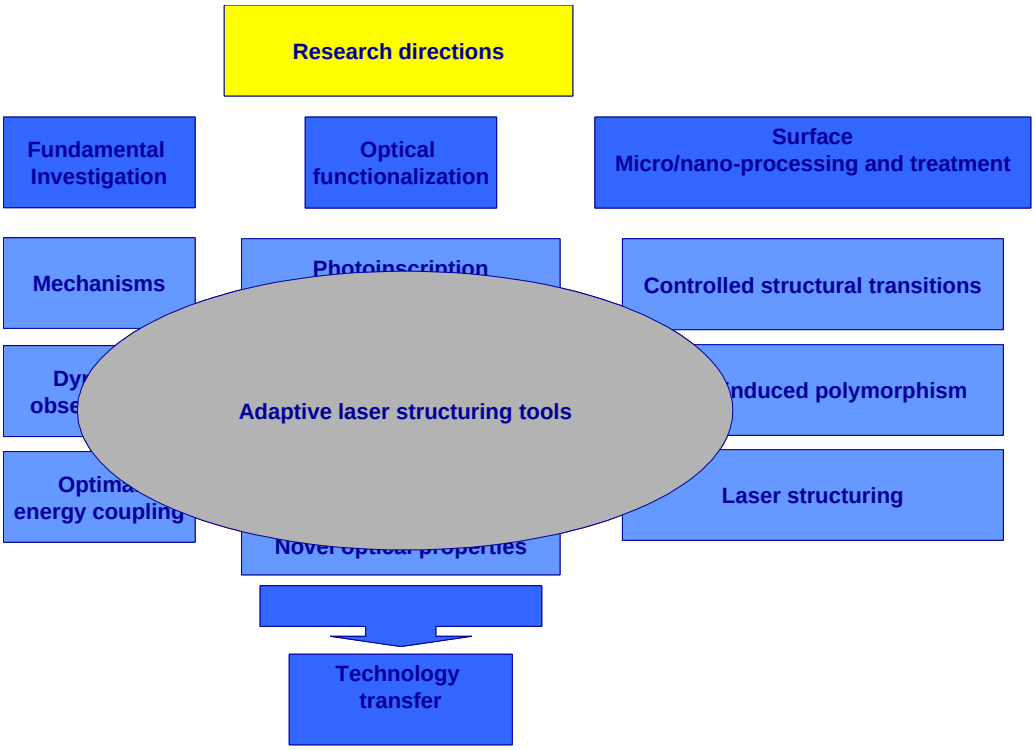

Figure Introduction 2: Schematic structure of the research activity.

A quasi-chronological description of the research activity, underlining the main scientific accomplishments, is presented in the following sections, which follow the experimental logic and organization of my scientific approach; mechanisms, dynamics, irradiation design for optimal interaction. The physical rationale is given, together with the presentation of experimental concepts used to probe energy deposition, interrogate transformation mechanisms, visualize their dynamics, and develop control loops. The results were obtained in different financial frames, provided by Federal Ministry for Education and Research and the German Research Foundation, with a significant contribution in the last years by the French Research Agency in the frame of a Junior Chair d'Excellence.

The work is organized as follows. Chapter 1 presents in a brief manner the main irradiation factors which contribute to absorption and to subsequent generation of various ablation phases at material surfaces, including the kinetic depiction of the properties of ejecta. Emphasis is put on describing the electrostatic ejection of ions from dielectric surfaces as well as on the onset of thermal components in the kinetic distribution of the emitted particles from metallic and semiconductor surfaces. As theory is central to understanding key features of interaction, a short description of our theoretical approach is given, from laser coupling into non-transparent materials to nonlinear pulse propagation in dielectrics. Chapter 2 follows in time the energy relaxation dynamics in various materials, indicating the relevant characteristic times. The dynamic interrogation of excitation is made at surfaces and in the bulk, in the conditions of energy confinement. The following Chapters take advantage of this dynamics, introduce the concept of spatio-temporal beam engineering and laser-material synchronization, and indicate the potential of adaptive processing techniques. Examples are given concerning controlled phase transitions and thermodynamic trajectories at non-transparent interfaces, and will be extrapolated to designed refractive index changes for photonic applications. The narrative follows the schematic representation illustrated in the second figure. Synthesizing the accumulated knowledge, a summary and perspective section will end up the description. The chapters are organized to emphasize the framework of the presented research results, providing the problematic, the motivation, the scientific logic and context, followed by a brief argumentation of the observed factors and conclusions. For the full scientific rationale, the corresponding published articles are joined. The bibliographic list in this work is not exhaustive, nor was it intended to be, since it serves to locally illustrate development tendencies. For a more complete review of the international situation and the present efforts, the reader is requested to refer to the comprehensive reference lists within the corresponding articles.

The final annexes present a synopsis of the published activity and, as well, a description of my involvement in scientific management, project coordination, cooperative research actions, educational activity or actions of technology transfer.

Chapter 1: Primary effects of laser irradiation

Inspected from a time perspective, my involvement in the laser ablation activity started with two main directions; the study of optical damage and the development of laser processing techniques. Within this framework, the present chapter emphasizes some general characteristics and driving factors for ultrafast laser ablation of solid matter, with a focus on laser interactions with dielectric materials. Small band-gap materials and opaque materials (e.g. metallic surfaces) will be treated as well. After a general introduction in ultrafast laser absorption, a discussion on incubation effects is given, followed by a description of the relevant ablation phases. Incubation is considered, among other factors such as pulse duration and pulse energy, as being the main control knob, regulating the ablation phases and the transition between non-thermal and thermal behaviors. The discussion concentrates on the kinetic properties of the ejecta, which allow mechanistic deductions on the main emission factors and precursors. The narrative will follow with examples of processing bulk materials.

1.1 Laser excitation of materials, brief overview

A considerable amount of work deals with light-induced electronic excitation and, usually, the following general irradiation picture emerges. The laser energy is deposited into the irradiated sample via electronic excitation. This includes free electron absorption for metallic materials by collisional mechanisms involving third party partners [LZC08]. On the other hand, multiphoton excitation, respectively tunneling auto-ionization [Kel65] by direct interband transitions or defect-mediated was observed in band-gap materials, being followed by inverse Bremsstrahlung and a subsequently seeded collisional carrier multiplication [SFP95, KRS00, Gru07] before further dissipation. The energy quantity acquired in the two sequential steps, photoionization and free carrier absorption, offers the possibility of regulating the amount of energy coupled to the material, the transient optical properties, and the outcome in terms of possible transformation paths. The absorption efficiency is controlled via the photoionization cross-section and by the timescale of electronic collisions and momentum scattering. Subsequently, the electronic energy is relaxed into the material matrix by an electronic-vibration coupling mechanisms which locally heats the material, via bond-softening and atomic displacements caused by electronic perturbations of the matrix, or is released by a pressure-induced mechanical activity. If the deposited energy may diffuse in time without visible permanent effects, in many cases, sub-threshold perturbation of the pristine materials will preserve a memory effect of the initial irradiation [RGC06].

1.2 Processing of materials with ultrashort laser pulses

A main drive for laser applications was constituted by material processing technologies [CMN96]. During the stay at MBI as a graduate student, an application-oriented evaluation for material processing was developed. The main objective was to perform a survey of the potential of applying femtosecond laser technology for material processing. It was shown that ultrashort laser pulses can be used to fabricate with high degree of precision long channels and micro-holes, where the choice of specific laser pulses has a significant influence on the quality of the induced structures [Sto00]. The possibility of going below the diffraction limit was equally explored, based on the highly nonlinear character of interaction in band-gap materials. A description of possible modifications in transparent materials using ultrashort laser pulses in different regimes is depicted in Fig. 1-1. The choice of the operating fluence and irradiation dose determines the relevant structuring process.

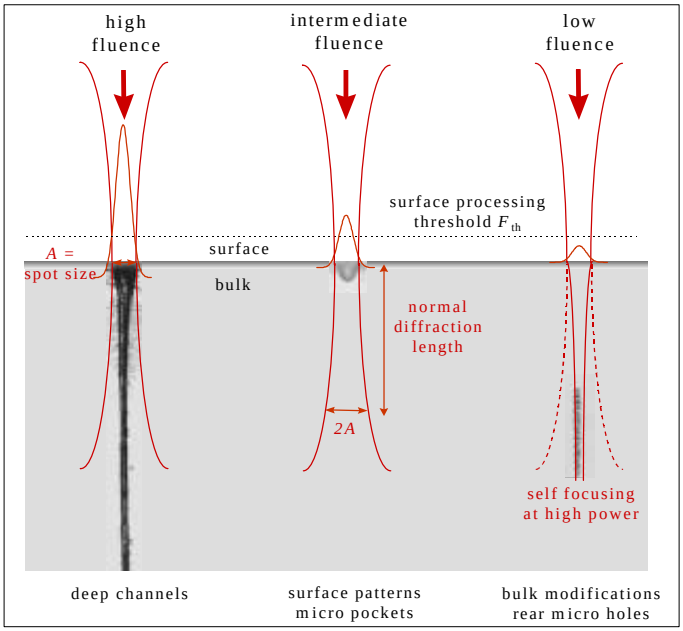

Fig. 1-1: Schematic diagram of major fluence regimes for material (dielectric) processing in a side view perspective: high fluence for deep-drilling, intermediate fluence for surface patterning, low fluence for bulk modifications and rear side micro-holes using self-focusing effects.

1.3 Optical damage and incubation at surfaces

A problematic of interest at the time was related to optical damage mechanisms, investigating not well understood aspects of optical breakdown. Optical damage thresholds [Cha94] have considerable importance in designing optical components resistant to the action of ultrashort high intensity laser pulses and in the development of waveguiding or photonic structures in optical media [DMH96]. Studies of laser-induced optical damage in dielectrics also offer valuable information on the mechanisms responsible for optical breakdown in initially transparent materials, which were mainly related to electronic excitation above a

critical threshold and the onset of absorptive phases. A plethora of processes concurs to the point of material collapse, which include nonlinear plasma generation and non-equilibrium phenomena related to overcritical heating, when highly absorbing states are developed. If the initial perspective was concentrated on the interplay between direct photoionization and avalanche [LKS98, TBK99, QGM99], new insights developed more recently on the particular photoionization paths [SSW03, TSL06]. From the results obtained in the "Ultrafast material processing group" at MBI with the direct involvement of the author during the doctoral stay, the following picture arises on dielectrics [ASR00-14, RLS99-16, Sto00].

1. The optical damage threshold depends on the pulse duration, indicating the interplay between multiphoton and avalanche processes. A slow decrease in the sub-ps domain consistent with the multiphoton seeded collisional multiplication is observed.

2. A decrease of the laser-induced damage occurs at sites undergoing repetitive irradiation caused by incubation effects with increasing dose and related to the presence of defects. This depends on the time and strength required to complete the energy transfer cycle.

If this is a simplified description of the incubation process, the consequences are important. The effect of incubation [Mag90] is twofold: 1) It modifies the absorption cross-section through defect accumulation. 2) It induces additional routes for energy deposition into the lattice at localized sites, besides the non-selective electron-phonon coupling, routes that are based on trapped electrons coupled to the lattice. The increased photoionization efficiency leads to an electron density derived from defect sites, which is regarded as an additional contribution to the electron population originating from multiphoton absorption from the valence band. This contribution triggers the subsequent avalanche and affects the measured damage thresholds, showing an exponential decay with the pulse number per ablation site.

The origin of incubation is still ambiguously identified, fatigue, thermal stress and strain load, as well as increases in the local volume arising from defect production and bond-breaking can have additional influence. At the same time, the origin of defect centers is strongly dependent on the nature of the material and the lattice deformation induced during electron transport.

1.4 Onset of ablation phases

In that concerns surface irradiation (which initiates the first description of results in this work), dielectric ablation is usually associated with the peculiar appearance of two ablation phases that can be discriminated via their appearance (roughness), ablation rate, or the kinetic characteristics of the corresponding ionized ejecta. The ablation process develops

in different phases as a function of the laser fluence, pulse duration, and number of pulses per site. The initial gentle phase is characterized by smooth surfaces, high degree of ionization in the plume, and low ablation rates (few nm/pulse). The strong phase reveals greatly increased roughness and characteristics of a violent process for material expulsion of thermal nature. These visual aspects come together with one order of magnitude increase in the ablation rates and lower mean ionic energy along with plume thermalization. The significantly different appearances depicted in Fig. 1-2 for sapphire (where the phases are particularly visible) suggest the occurrence of several mechanisms of material expulsion, ranging from electronic transitions to nucleated explosive boiling. The process governing the transition between these two phases is mainly controlled by incubation. The transition from the gentle to the strong phase as well as the kinetic ejection of particles in these conditions constituted one of the main chapters of my doctoral work at the MBI Berlin.

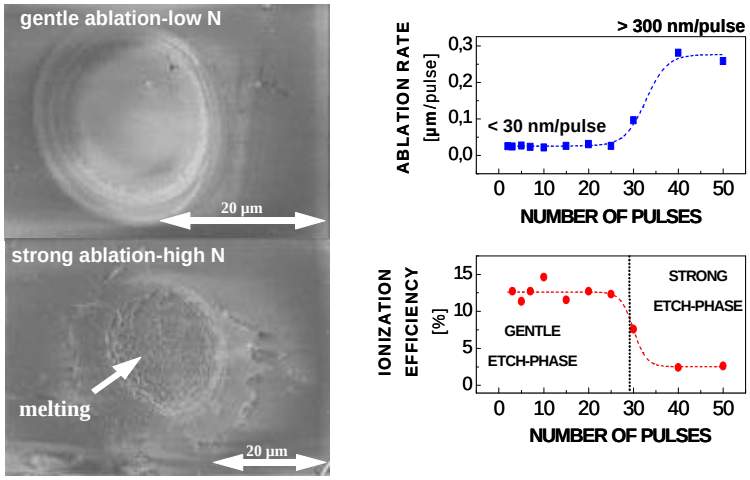

Fig. 1-2: Onset of ablation phases. (Left) Scanning electron microscope appearance of the gentle (N=10) and strong (N=30) phase in sapphire. (Right) Corresponding ablation rates and ionization efficiency. Irradiation conditions: pulse duration 0.2 ps, fluence 4 J/cm^2.

1.5 Mechanisms of laser ablation, non-thermal and thermal effects

Competition of electronic and thermal relaxation channels was already observed to play a role in structural transitions in materials with high electronic correlation. Here we are concerned with material removal mechanisms. Besides the inspection of the residual trace, further information was gathered by analyzing the emission products from a kinetic perspective. Studies of ablation mechanisms **on dielectrics** with ultrafast laser pulses via the investigation of the kinetic properties of ejecta have shown several characteristics [SAC00-11, SAKC00-12, SVC00-13] based on the balance between the non-thermal and thermal effects. Using time-of-fight (TOF) mass spectrometry on targets irradiated above the ablation threshold we have attempted to probe the nature of emission and to indicate a qualitative behavior of particle ejection.

The major finding was the onset of an impulsive, electrostatic break-up of the surface in the initial gentle phase, leading to high kinetic energies and mass-independent, charge-scaled momenta for the emitted ions (Fig. 1-3). Based on the most probable velocities, the characteristic momenta of Al^+ and O^+ were measured and shown to be equal. The origin of this mechanism results from the accumulation of uncompensated charge in the first monolayers due to photoionization, build-up of critical electrostatic surface energy density, and, in the absence of fast charge transport and neutralization, subsequent impulsive surface disintegration. Moreover, mass-resolved time-of-flight investigations have shown increased energies for the dielectric ions in comparison to the emitted neutrals or to the ions emitted from metallic surfaces. Electron emission studies indicated a fast component that originates from direct photoemission, alongside a slower component consisting of the electrons emitted with a certain delay with respect to the initial excitation and trapped by the positive charge in the plume, as shown in Fig. 1-4. All these arguments allowed us to formulate the hypothesis of the macroscopic electrostatic ion ejection (Coulomb explosion CE) from dielectrics which triggered additional studies and efforts in the laser ablation community.

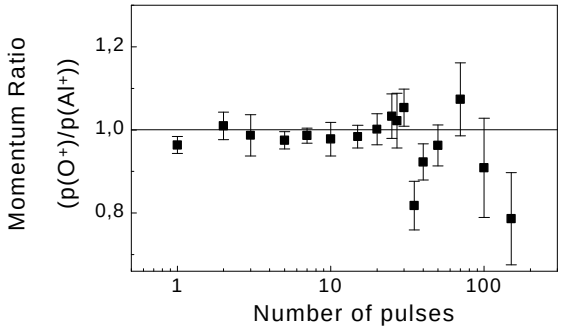

Fig. 1-3: Ratio of characteristic momenta from measured velocity distributions of O^+ and Al^+ ions emitted from sapphire samples. Irradiation conditions: pulse duration 0.2 ps, fluence 4 J/cm^2.

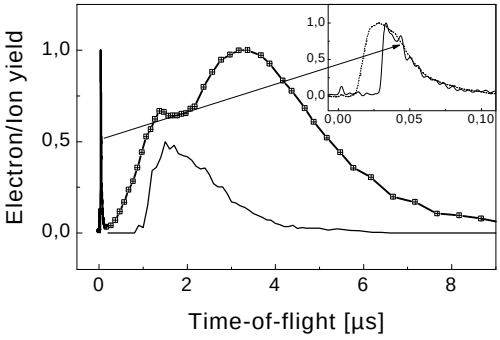

Fig. 1-4: Electron TOF data for sapphire (Al_2O_3), showing prompt and plume electrons. Solid line depicts the TOF of the positive ions, showing that the plume electrons have velocities comparable to the ions in the ablation plume. Insert: expanded scale for the prompt electrons. Full line: from Al_2O_3, dashed line from metallic Al. Irradiation conditions: pulse duration 0.2 ps, fluence 4 J/cm^2.

Following a collaborative program with N. Bulgakova (Institute of Thermophysics, Novosibirsk) we have made a rigorous attempt to theoretically model the Coulomb explosion

process [BSC04-7, SRC02-9] based on detailed description of ultrafast carrier transport in femtosecond-excited materials. The procedure relays on solving the carrier transport equation using a continuum drift-diffusion approach for different classes of materials, describing charge gradients induced by photoemission and carrier diffusion. The modeling provided further arguments to establish the concept of Coulomb explosion [BSC05].

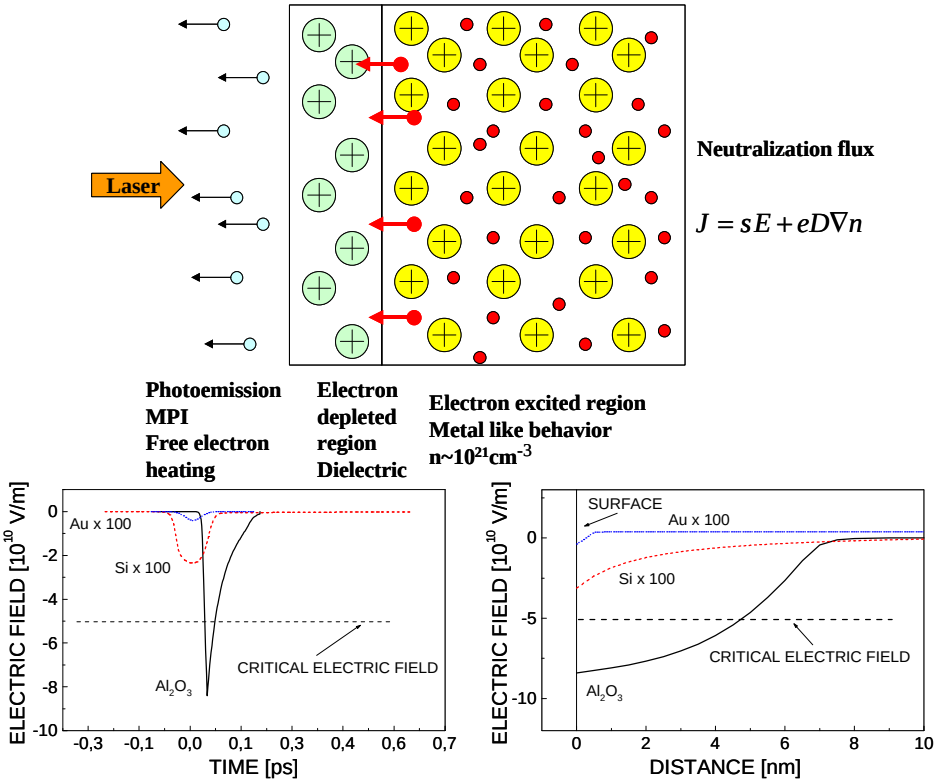

Fig. 1-5: Schematic representation of Coulomb explosion (top). Calculated spatio-temporal laser-induced electrostatic fields using a drift-diffusion approach (bottom, left and right). Irradiation conditions: pulse duration 0.2 ps, fluence 4 J/cm^2.

To shortly summarize the discussion above, the result indicated a considerable charging effect on dielectric materials, leading to the electrostatic rupture of the superficial layers. The characteristic quasi-electrostatic field (Fig. 1-5) induced by charge separation following photoemission and charge gradients has a sub-ps timescale and few nm bulk penetration depth. A disintegration criterion based on comparing the stored electrostatic energy to sublimation heat (a measure of bonding strength) was established. For materials with high carrier transport effectiveness such as metals and semiconductors, the charged field was found to be below the critical threshold. One should note that fast ion emission was observed recently also from metals [SHB00]. One of the hypotheses put forward, besides the localized charging at defect states [DLD94, KNT02], was based on generation of high fields at nanoscale protuberances relying on an optical rectification mechanism [VDS07]. However, there is still a certain disagreement on the CE occurrence on conductive materials [RJK03, SRC04]. Experimental techniques showed recently a promising possibility to timely-resolved

interrogate surface charging by fast electron beam deflection [HSM08], with the potential to address the issue of laser-charging of materials and electrostatic ablation on ultrafast scales.

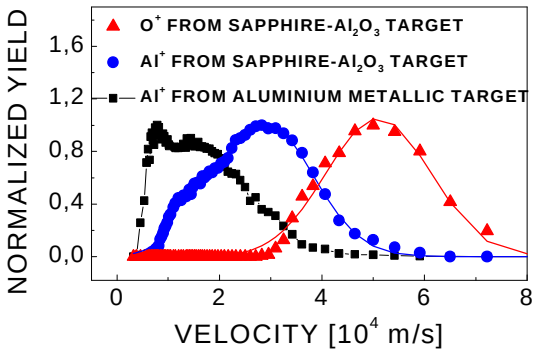

Fig. 1-6: Velocity distributions of ionic and neutral aluminum atoms removed from sapphire samples. Irradiation conditions: pulse duration 0.2 ps, Fluence 4 J/cm^2.

At higher irradiation doses or by augmenting the input laser fluence, the kinetic energy of the ablated ions decreases in the strong phase. Thermal effects start to become significant, shifting the balance towards heat-based ablation mechanisms. In this case, defect states act as trapping centers strongly coupled to the lattice, thus additionally contributing to the lattice heating and phase transformation. The high temperatures achieved during the ablation process indicate that the most probable mechanism is phase explosion resulting from homogeneous nucleation. Other thermal processes are kinetically limited, namely vaporization rates are extremely low and normal boiling is too slow. The developed model offers additionally criteria for the establishment of thermal equilibrium. The kinetic properties of ions emitted from metals and semiconductors (Fig. 1-6) show the development of low-velocity components, presumably of thermal nature. The question on the possibility of accelerating low-velocity particles by enhancing thermal effects will be treated in Chapter 4.

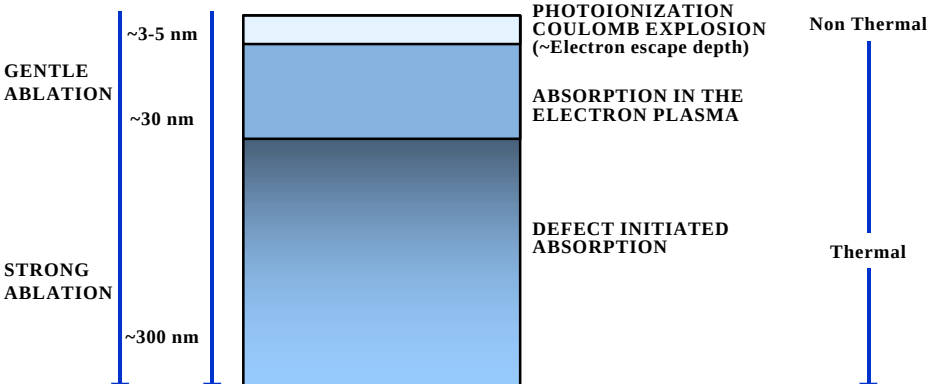

Fig. 1-7: Overview of the ablation phases during ultrashort pulsed laser ablation of dielectrics.

As a short conclusion, all these characteristics indicate that most of the deposited laser energy is retraced in the kinetic properties of the ejecta rather then as residual thermal energy into the sample. Studies were performed in various conditions of irradiation, varying the pulse

duration, energy, and the irradiation dose. The efficiency of the material transformation to the gas phase depends on the particular ablation stages and on the time characteristics of the laser pulse, which, together with the laser energy and the irradiation dose, are able to tune the balance between thermal and non-thermal mechanisms. An overview of the developments of the ablation phases is given in Fig. 1-7, summing up the main key points of the discussion above; photoionization, electronically-mediated emission of ions, incubation, the change in absorption by plasma or defect coupling, and the gentle to the strong phase transition.

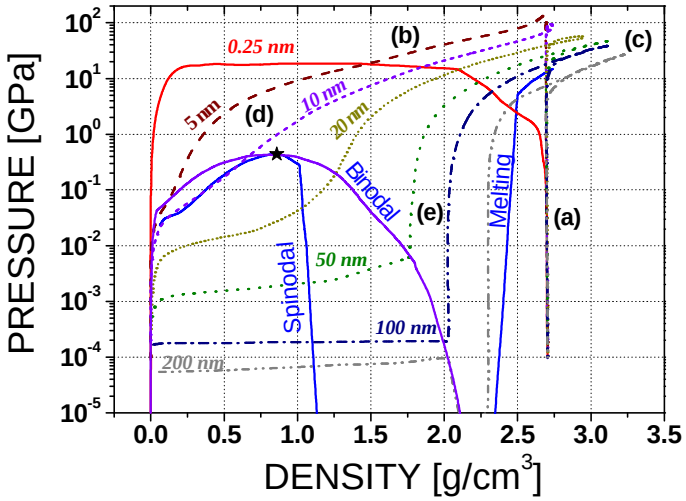

Fig. 1-8: Typical thermodynamic trajectories in the pressure-density phase diagram of aluminum exposed to ultrafast laser radiation of 150 fs, and 5 J/cm^2. Thermodynamic paths of particular material layers are plotted for several depths inside the metal.

More recently, ablation of **metals** become a topic of research of its own, rather than a comparison factor for dielectric ablation. Concerning the ultrafast laser ablation of metallic surfaces, a hydrodynamic code developed by J. P. Colombier (lecturer at the Jean Monnet University) is being updated to describe the thermodynamic evolution of the excited matter, from the solid down to the plasma phase, as well as the generation of shock waves in the material [CCA07]. This involves a Lagrangean code, well adapted to study material deformations and to follow in time the thermodynamical state of the system. The approach couples optical, thermal, and mechanical models, reproducing multiscale processes related to matter transformation and gathering non-equilibrium excitation and transport formalisms into a unitary fluid code. A special emphasis was put in accurately describing electronic collisional processes involving light on different timescales corresponding to various evolution stages. The code follows the primary electron heating, the generation of non-equilibrium states leading to ablation, complex thermodynamic trajectories, material removal and recast. Fig. 1-8 shows typical thermodynamic trajectories of laser irradiated aluminum after a sudden, quasi-isochoric excitation. The attached references provide the necessary details with respect to the excitation processes (the nonlinear dynamics given by the Pauli's exclusion principle

and Coulomb screening, the subsequent electron-phonon interaction, etc). The ablation process was observed to be always mediated by the liquid phase. The phase transformation, expansion of critical fluids, the mechanical fragmentation, as well as the mechanical fracture of the solid and its spallation were described with high accuracy via multiphase equations of states [CCA07]. One of the main consequences was related to a deeper understanding of material specific transformation paths as well as the dynamics of a potentially more universal phenomenon. Particular aspects will be treated in the following chapters.

1.6 Nonlinear focusing and Incubation in the bulk

The laser processing procedures advanced towards structuring the bulk of the materials, with a specific accent on inducing embedded structures with particular optical functions and variable dielectric constants. At the initial moment of this research activity and confirmed by the tremendous progress afterwards, the technique was considered potentially interesting for processing bulk materials for optical functionality and data storage applications [GMH96, GM97]. Optical Kerr nonlinearity and the associated spatial self-focusing of Gaussian beams can induce bulk modifications in solid transparent media without affecting the entrance and exit surfaces. The temporal and spatial propagation effects are connected by the material response. The catastrophic collapse of the beam is usually arrested by the onset of ionization which channels the light in the interaction region. The fluence augments during the propagation because of the spatial focusing until the threshold value is reached in the form of point defects, coloration, or micro-explosions. Fig. 1-9 shows micro-modification in bulk-SiO_2 as a function of the number of shots per site and three different pulse durations in the sub-ps and ps range. The results generally indicate strong self-focusing, however an exception exists for sub-ps pulses where defocusing on the laser-induced free electron population and group velocity dispersion counter-balance the Kerr nonlinearity [Gae00, SCM02].

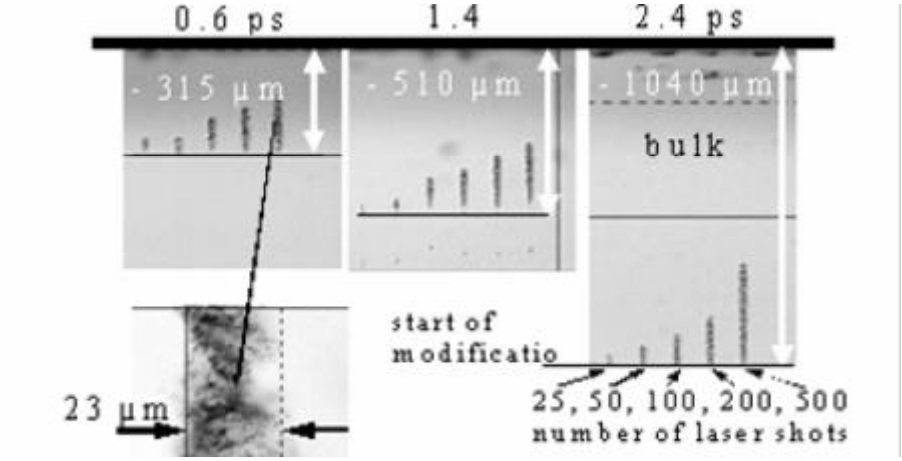

Fig. 1-9: Optical microscope pictures of laser induced modifications in the bulk of fused silica samples as function of pulse duration. The radiation is focused on the surface.

1.7 Functionalization of transparent materials for optical applications

The last years put forward a tremendous research and development effort for functionalization of optical materials with the aim of controlling light transport in optical systems. Among various techniques, laser-induced 3D photoinscription opens up new perspectives for emerging photonic applications, namely embedded optical functions such as guiding, amplification, coupling, diffraction, which developed into a major field of applications [WAN03, SBL05, DTL07, ZEH07]. The particular strong energy localization due to ultrafast laser pulses has provided a significant momentum to this field. The main drive is to design dielectric properties on mesoscopic and macroscopic scales and add specific optical functions to compact, integrated optical devices. The foundation lies in local changes of the refractive index which constitute the building block of embedded photonic functions. Within this field we have concentrated on key questions concerning the nature and the distribution of refractive index changes inside the bulk of various glassy materials in relation to the material properties and the excitation channels. The development was made in the frame of two PhD theses, A. Mermillod-Blondin and C. Mauclair. Several highlights, results and implications are discussed below.

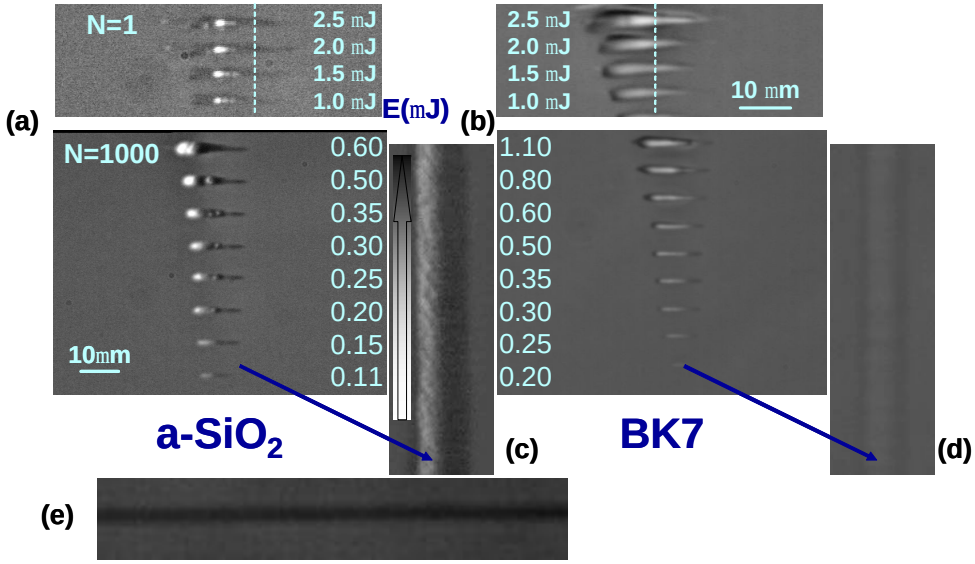

Fig. 1-10: Single and multishot static irradiation traces induced by ultrashort laser pulse at 100 Hz repetition rate and various energies for different materials, (a) a-SiO_2 and (b) BK7. Dominant positive refractive index changes (dark colors) are obtained for a-SiO_2, in contrast to BK7 which shows a preferential index decrease (white colors). (c, d) Traces obtained by transverse scan of the focal point are indicated. (e) High speed longitudinal trace in *a*-SiO_2 (20 kHz, 19 mW, 750 µm/s). Observations in phase contrast microscopy.

It is know that ultrashort laser pulses focused inside transparent materials can induce local variations of the optical properties [SCM02]. Irradiation creates physicochemical material changes, building up on deviations from charge, thermal, or mechanical equilibrium. The high absorption nonlinearity leads to the bulk development of an electron-hole plasma by

complex photoionization events. The subsequent relaxation depends on substance nature and results in electronic and structural alterations associated with either increasing or decreasing the refractive index under light exposure. Fast energy deposition is then able to induce unique structural material phases due to extreme pressure and temperature regimes generated inside the material [JNO06].

The formation of an embedded phase object is associated with bond breaking and reordering resulting from changes in density, accumulation of stress, and the appearance of color centers [MGP97, CHK01, SB02, ZRS05] which can be caused by electronic and thermal effects. Positive refractive index changes resulting from the rearrangement of the dielectric matrix [KO04, BSZ05, EKT04, ZXR04, JNT06, LJG05] are essential factors for laser waveguide writing techniques. If, for example, positive variation of the refractive index is easily obtained in a-SiO_2 where the material quenches in a densified form involving a change in the bonding angle [CHK01], the response of complex multicomponent glasses is more difficult to be deciphered [BSZ05, EKT04] and the result of the laser action is equally defined by the material character (specifically the rate of energy relaxation in electronic, thermal, and mechanical forms) and the spatio-temporal characteristics of the exciting laser pulse. Depending on the irradiation dose and scale of energy confinement, local atomic displacements concur with macroscale phenomena in a complex way to generate a refractive index change. Low irradiation doses initiate refractive index changes which rely on defect formation and local densification, while high irradiation input triggers macroscopic thermomechanical mechanisms for rarefaction and compaction. Consequently, we have developed techniques to observe and interrogate the formation of refractive index changes.

a) Experimental development: Using phase-contrast microscopy techniques we have studied the spatial distribution of refractive index changes in various materials and correlated the observations with the nonlinear pulse propagation and with the optical and, specifically, the thermo-mechanical properties of the transparent material. Zernike-type phase-contrast microscopy is a natural way to visualize phase objects with low absorptivity contrast. Consequently, the laser-induced phase object can be identified and the refractive index change can be estimated relative to the background. Phase microscopy generates specific shifts in the illumination path and, using constructive/destructive interference, transforms phase differences into intensity contrast, and delivers a color map which is related to changes in the dielectric function. The dark colors in the microscope image correspond to positive refractive index variations while the white colors indicate a refractive index decrease or the apparition of scattering centers. The relative variation of the refractive change can be correlated with the

amount of deposited energy and, subsequently, with the material expansion coefficient. We have observed an index decrease at high energy loads or in materials with high thermal expansion characteristics and regions of dominant positive refractive index increase in materials close to fused-silica structure. An example of laser-induced structures in a-SiO_2 and BK7 is given in Fig. 1-10. However, in many cases the index change is spatially modulated, with alternating regions of positive and negative variations [MBH06-5]. Usually, the negative index change correlates with regions of high energy concentration where high-pressure hot regions are generated. These regions are the consequence of the geometrical aspects of tight focusing with nonlinear self-focusing contributions [BBH07-3]. Shock wave generation, rarefaction, and cavity formation were investigated as well.

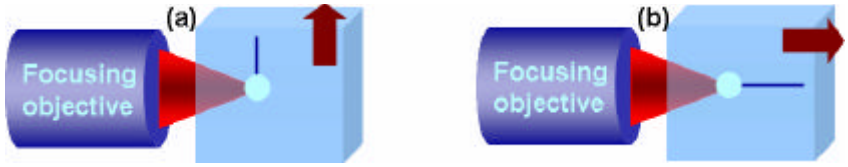

Fig. 1-11: Irradiation geometries indicating (a) transverse and (b) longitudinal waveguide writing strategies using laser photoinscription. The scan direction is indicated by the arrow.

Optical transformation of transparent materials stimulated growing interest in designing embedded structures with optical functions. One notable development, translating the focused beam inside the material is able to replicate the structural change and to induce traces of refractive index modifications with waveguiding properties. Transverse or longitudinal photoinscription strategies were established based on the scan direction relative to the laser beam (Fig. 1-11). Each particular strategy has its own advantages and disadvantages concerning the symmetry of writing and the length of the trace. Mode symmetric waveguides can be longitudinally written but limitations appear with respect to deep focusing in the bulk and associated aberrations. The transverse scan allows traces of arbitrary length. Astigmatic forming of the beam can compensate the asymmetry induced by the focal elongation in the confocal region [OTC03, FDS07, AMW05].

From the experimental point of view, several strategies were put forward for waveguide writing. Low repetition rates (kHz) were often used, building up on the effect of individual pulses [CHK03, NBT03]. High repetition rates (MHz) were more recently involved, taking advantage on cumulative thermal effects [SBM01, EZH05, OCP05]. The intermediate region (100 kHz), corresponding to the timescale of stress relaxation was equally explored for generating waveguiding structures in several materials [MOH97, BSZ05]. As mentioned, the waveguiding capability depends strongly on the material properties and the characteristics of pulse excitation. This leads to specific challenges in determining processing

windows leading to positive refractive index along the trace, challenges that have to take these factors into account. Generating positive index changes has then important consequences for the photoinscription of efficient, low-loss waveguiding devices, as well as for more complex systems with advanced photonic functions.

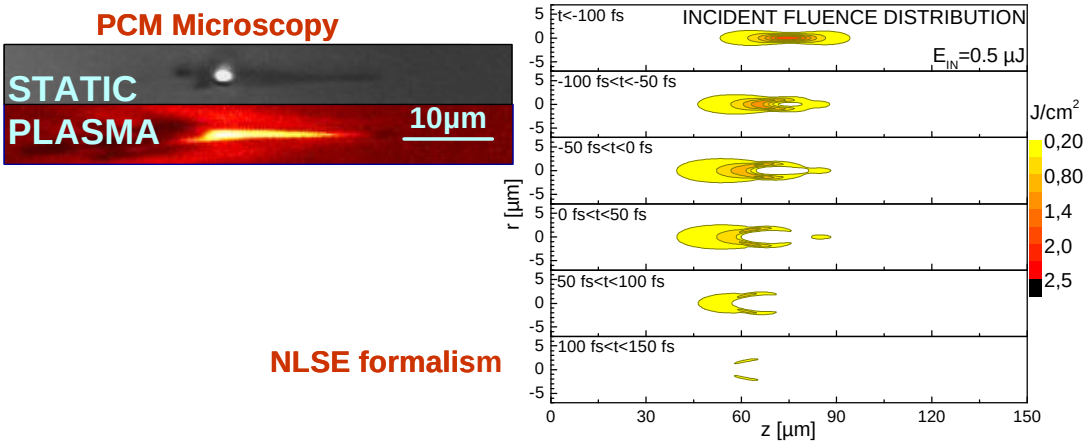

Fig. 1-12: Phase contrast microscopy (PCM) image of single pulse interaction result (index change pattern) in fused silica (left) together with plasma images, and simulation of nonlinear energy irradiation (right). Irradiation conditions: single pulses 120 fs pulse duration, 1 µJ input energy.

Theoretical development: The propagation of ultrashort laser pulses in transparent environments is commonly associated with the onset of significant nonlinear effects and self-actions of the laser pulse. A nonlinear pulse propagation code based on the nonlinear Schrödinger formalism (NLSE) was developed together with I. Burakov during his postdoc stay to study in a time- and space-resolved way the excitation footprints, the regions of energy deposition as well as the associated spectral alteration of the crossing pulse upon focusing in glassy materials. The approach takes into consideration key features of pulse propagation and material excitation such as self-focusing, phase modulation and defocusing on carrier plasmas. Further effects include diffraction, multiphoton and avalanche ionization, group-velocity dispersion, space-time coupling, and energy losses on the free electrons. A particular result is presented in Fig. 1-12, showing the dynamics of energy input in the first moments of interaction [BBH07-3]. The main observation relates to a shift in the energy deposition area towards the pulse direction which generates an axially modulated index structure. The code has allowed establishing connections between the spatial distribution of energy and the observed two-dimensional map of laser-induced modifications, notably refractive index changes. Non-paraxial corrections to the NLSE equation were developed as well.

The code was supplemented by thermo-mechanical calculations performed during a joint program with Y. Meschsheryakov (Institute of Hydrodynamics, Novosibirsk) and N. Bulgakova (Institute of Thermophysics, Novosibirsk). A thermal elasto-plastic Lagrangean

model was developed to follow deformations in irradiated glasses and to determine the material density transformations. The model is succinctly described below. The energy deposition footprint is determined by the nonlinear propagation code. The absorbed energy, which is equivalent to an instantaneous temperature field, evolves in time according to the material thermo-mechanic properties. This assumption is justified as long as the energy transfer to the glass matrix occurs on a picosecond scale, much shorter than the mechanical response. Due to the fast relaxation, the material follows a quasi-isochoric path to the hot state, which subsequently cools by diffusion. In calculating the induced stress, the approach based on the finite element method combines standard equations of dynamic elasticity [Tim72, Wil64, MB06], the equations of motion, and the Hook's law with the von Mises yield criterion for plastic yielding, and allows us to model structural deformations inside the heated material. Stress tensor components are calculated assuming cylindrical symmetry. The model takes into account phenomena such as heat transfer, dynamic elasticity, and material deformations with plastic yielding. It iteratively follows the changes in temperature and the subsequent variations in the stress and density fields in the assumption that glass viscosity is large enough and cooling takes place without strong elastic waves. In view of the complexity of the approach and the present knowledge of material parameters, the model gives a qualitative indication of material behavior trends under laser excitation [MBS08]. At the same time, the model offers a view into the relevant timescales, the fast nanosecond rarefaction or the subsequent material return upon cooling on microsecond scale.

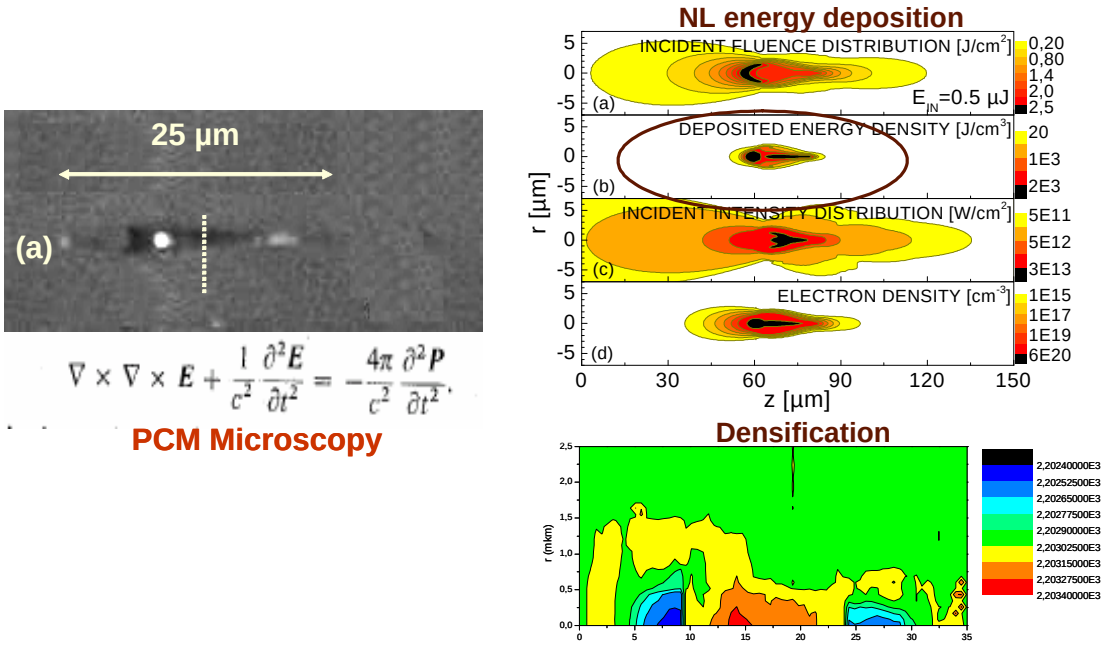

Fig. 1-13: Phase contrast microscopy (PCM) image of single pulse interaction result (index change pattern) in fused silica (left) and simulation of nonlinear energy irradiation (right) together with thermoelastic simulations of material densification (bottom). Irradiation conditions: single pulses 120 fs pulse duration, 1 µJ input energy.

An example of spatially distinct laser-induced densification and rarefaction domains is given in Fig. 1-13, showing the rarefaction zones following initial thermal expansion in the regions of high initial energy concentration, as well as compaction in the median region during cooling and relaxation of elastic stresses from the surrounding, elastically compressed region. Further details concerning the numerical approach will be given in Chapter 4, when the consequences of the repetition rate at different pulse shapes will be discussed.

b) Direct observation of refractive index change: A numerical and experimental parametric study of the effect of pulse duration, number of pulses, and focusing conditions on the aspect of laser induced dielectric changes was realized for various materials relevant for optical applications (silica-based glasses, phosphate glasses, heavy-metal oxide materials). The study indicated the regions of preferential energy deposition along the propagation axis, interrogating as well the corresponding index change in axially modulated structures. The qualitative phase-contrast microscopy was combined with quantitative phase microscopy (QPM) in cooperation with RWTH Aachen and, as will be seen in the next Chapters, with time-resolved imaging techniques.

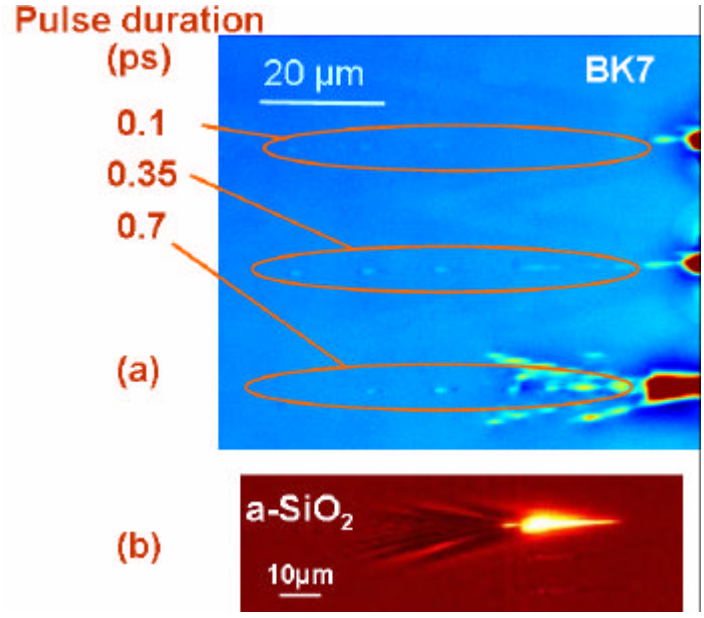

Fig. 1-14: (a) Phase contrast microscopy (PCM) image of high energy (15 µJ) single pulse interaction result (index change pattern) in BK7. Regular structures are formed in the wake of the focused pulse as a function of pulse duration. (b) Electron plasma images in ultrashort pulsed laser-irradiated fused silica at 10 µJ input energy. Light is focused in different cones (NA=0.45).

The high spatial resolution permits discerning fine focusing details, artifacts of tight focusing in the presence of wavefront distortions, able to create a kaleidoscope of regular traces and array of spots in the wake of the laser focus (Fig. 1-14).

c) writing waveguiding structures: We have optimized the laser writing parameters for generating smooth waveguiding structures in fused silica, considered here as a reference

material. The optimization window involved extrinsic parameters such as laser energy, scan velocity, focusing conditions, and the laser repetition rate. An example of waveguiding structures realized in fused silica is given in Fig. 1-10.

1.8 Summary

This chapter indicated that useful information can be extracted with respect to material ablation and modification channels by analyzing the spatial topology of the residual trace at surfaces or in the bulk and the kinetic characteristics of the ablation products. Indication was given concerning specific energetic channels promoting material removal for different classes of materials which strongly depend on the absorption characteristics and the effectiveness of relaxation. Electronic and thermal mechanisms were proposed to explain the observed material transformations, with a practical perspective on the laser-induced optical damage. Elements were given to illuminate the surface breakup undergoing an impulsive electrostatic disruption in dielectric materials, prior to the development of thermal channels of transformation to the gas phase. For metallic surfaces, thermodynamic trajectories were followed as well, indicating how finite amounts of material are affected as a function of specific energy relaxation channels and the effectiveness of the electronic transport. Insight was delivered into laser-induced variations of the refractive index in bulk transparent materials, accompanied by relevant theoretical approaches. Conditions for processing efficient waveguiding structures were determined.

List of selected papers for presentation:

1) N.M. Bulgakova, I.M. Burakov, Y.P. Meshcheryakov, R. Stoian, A. Rosenfeld, and I.V. Hertel “Theoretical Models and Qualitative Interpretations of Fs Material Processing” J. Laser Micro-Nanoengineering 2, 76 (2007)

2) J.P. Colombier, P. Combis, R. Stoian, and E. Audouard “High shock release in ultrafast laser irradiated metals: A scenario for material ejection” Phys. Rev. B 75 104105 (2007)

3) I.M. Burakov, N.M. Bulgakova, R. Stoian, A. Mermillod-Blondin, E. Audouard, A. Rosenfeld, A. Husakou, and I.V. Hertel “Spatial distribution of refractive index variations induced in bulk fused silica by single ultrashort and short laser pulses” J. Appl. Phys. 101, 043506 (2007)

4) A. Mermillod-Blondin, I.M. Burakov, R. Stoian, A. Rosenfeld, E. Audouard, N.M. Bulgakova, and I.V. Hertel “Direct observation of femtosecond laser induced

modifications in the bulk of fused silica by phase contrast microscopy" J. Laser Micro-Nanoengineering 1, 155 (2006)

5) S.W. Winkler, I.M. Burakov, R. Stoian, N.M. Bulgakova, A. Husakou, A. Mermillod-Blondin, A. Rosenfeld, D. Ashkenasi, and I.V. Hertel "Transient response of dielectric materials exposed to ultrafast laser irradiation" Appl. Phys. A 84, 413 (2006)

6) N.M. Bulgakova, R. Stoian, A. Rosenfeld, I.V. Hertel, W. Marine, E.E.B. Campbell "A general continuum approach to describe fast electronic transport in pulsed laser irradiated materials: The problem of Coulomb explosion" Appl. Phys. A 81, 345 (2005)

7) N.M. Bulgakova, R. Stoian, A. Rosenfeld, I.V. Hertel, and E.E.B. Campbell "Electronic transport and consequences for material removal in ultrafast pulsed laser ablation of materials" Phys. Rev. B (2004) 69, 054102 (2004)

8) R. Stoian, A. Rosenfeld, I. V. Hertel, N. M. Bulgakova, E. E. B. Campbell "Comment on "Coulomb explosion in femtosecond laser ablation of Si.111" [Appl. Phys. Lett. 82, 4190 (2003)]" Appl. Phys. Lett. 85, 694 (2004)

9) R. Stoian, A. Rosenfeld, D. Ashkenasi, I.V. Hertel, N.M. Bulgakova, and E.E.B. Campbell "Surface Charging and Impulsive Ion Ejection during Ultrashort Pulsed Laser Ablation" Phys. Rev. Lett. 88, 097603 (2002)

10) I.V. Hertel, R. Stoian, A. Rosenfeld, D. Ashkenasi, and E.E.B. Campbell "On the physics of material processing with femtosecond lasers" Riken Review 32, 23 (2001)

11) R. Stoian, D. Ashkenasi, A. Rosenfeld, and E.E.B. Campbell "Coulomb Explosion in Ultrashort Pulsed Laser Ablation of Al_2O_3" Phys. Rev. B. 62, 13167 (2000)

12) R. Stoian, D. Ashkenasi, A. Rosenfeld, M. Witmann, R. Kelly, and E.E.B. Campbell "The dynamics of Ion Expulsion in Ultrashort Pulse Laser Sputtering of Al_2O_3" Nucl. Instrum. Meth. B 166-167, 682 (2000)

13) R. Stoian, H. Varel, A. Rosenfeld, D. Ashkenasi, R. Kelly, and E.E.B. Campbell "Ion time-of-flight analyses of ultrashort pulsed laser-induced processing of Al_2O_3" Appl. Surf. Sci. 165, 44 (2000)

14) D. Ashkenasi, R. Stoian, and A. Rosenfeld "Single and multiple ultra-short laser pulse ablation threshold of Al_2O_3 (corundum) at different etch phases" Appl. Surf. Sci. 154-155, 40 (2000)

15) D. Ashkenasi, M. Lorenz, R. Stoian, and A. Rosenfeld "Surface damage threshold and structuring of dielectrics using femtosecond laser pulses: the role of incubation" Appl. Surf. Sci. 150, 101 (1999)

16) A. Rosenfeld, M. Lorenz, D. Ashkenasi, and R. Stoian “Ultrashort-laser pulse damage threshold of transparent materials and the role of incubation” Appl. Phys. A: Matter Sci. Process. 69 (Suppl.), S373 (1999)

Chapter 2: Excitation processes and relaxation dynamics

If static investigations indicate possible paths of interaction, the physical picture can be complemented by following in time the respective mechanisms. In the recent years, significant progress was achieved in probing structural phase transitions and visualization of atomic movements with highest temporal resolution, employing optical or X-ray/electron diffraction techniques [SBA98, SCS99, RRH01, SDM03]. The time-resolved observations have allowed to identify ultrafast non-thermal channels for phase transitions, in competition to regular thermal transformations. The fundamental question arrives then on the relevant timescales of energy relaxation, the temporal development of the energy flow into the sample, which finally leads to ablation and material ejection. In the following sections, the discussion concentrates on time-resolved experiments concerning energy coupling and material transformation on picosecond timescales at surfaces and in the bulk. The relaxation times and the material structural conversion scales have an intrinsic value regarding the mechanisms of transformation. The sequence of transformation is equivalent to a change in the optical, thermal, and electrical properties of the materials. Consequently, the characteristic times can be useful for designing irradiation profiles that may take benefits from this implicit dynamics. As a follow up, we have developed spectroscopic and optical methods to probe the evolution of excited matter. The results description starts with a snapshot into the dynamics of particle emission and continues with observations of bulk excitation. The investigations have been performed during my doctoral period and continued in the frame of the PhD theses I had the pleasure to coordinate.

2.1 Dynamics of surface laser ablation

Initial transient experiments were dedicated to time-resolved mass spectrometry of the ablation products, with a focus on probing the mechanisms and dynamics of ion expulsion in the initial phases of excitation. The experiments were performed in an equal pump-probe configuration, where both pulses had sub-threshold intensities, while the correlated effect lied above the threshold. Ion emission was used as a probe for the accumulated superficial energy density. Time-resolved experiments on ion emission from femtosecond laser irradiated dielectric materials (Al_2O_3 and SiO_2), depicted in Fig. 2-1 and Fig. 2-2 indicated two regions of interest [SAC02-4], emphasizing the memory of excitation and the material dependent competition between non-thermal and thermal mechanisms. Depending on the ions kinetic characteristics measured in pump-probe experiments, several features were observed:

- a fast, non-thermal feature of sub-ps duration, originating in a Coulomb explosion of the surface. This electrostatic peak was observed only for dielectrics, while for metals and semiconductors neutralization of the excess charge occurs before lattice break-up. The fast dynamics is recognizable in Fig. 2-2 only for the dielectric materials, a large thermal component being indicated for Si. Time-resolved observations of the photoelectric yield indicated that the Coulomb explosion ion peak correlates with the direct photoemitted (prompt) electrons (Fig. 2-1). This situation largely resembles the ion sputtering features.
- a slower feature follows, being caused by a thermal mechanism on a time scale given by the electron-phonon coupling strength and heat transport efficiency; the thermal peak onsets at shorter times for SiO_2 compared to Al_2O_3 due to efficient electron self-trapping and increased electron-lattice coupling. In contrast to the fast ions indicating non-thermal mechanisms, measurements on slow ions have shown a thermal signature following the surface heating, caused by the energy transfer to the lattice. The behavior of metals and semiconductors emphasizes the thermal components in this low fluence irradiation regime, as well as the efficiency of electron-phonon coupling. The delayed increase in the ion yield is equivalent to a change in the coupling efficiency by surface heating and its eventual transformation to the liquid phase.

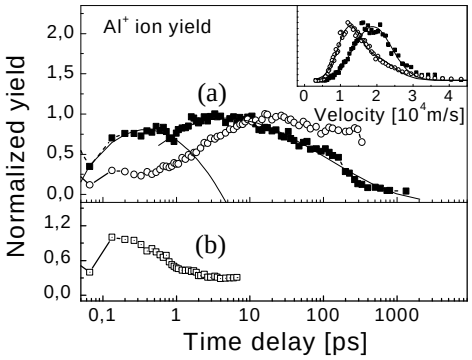

Fig. 2-1: (a) Fast (squares) and slow (circles) Al^+ yield ejected from a sapphire sample in a two sub-threshold pulse correlation pump-probe experiment as a function of the delay time. Insert: velocity distributions measured at two pump-probe delays: squares-0.6ps, circles-12 ps. (b) Time-resolved behavior of the direct photoemitted emitted prompt electrons in similar irradiation conditions.

- there is a material-dependent time for releasing the electron energy to the lattice (Fig. 2-3) and thermalization. For metals and semiconductors, materials with similar transport properties, the path to ablation follows a thermodynamic behavior regulated by the efficiency of energy transfer. The ion emission due to a thermally-induced transition to the gas phase shows lower velocity components as compared to dielectric materials.

It has to be mentioned that, at high energies, semiconductors commonly show a fast, electronically-induced transition to a disordered state due to phonon mode softening [JG03,

RRH01], with properties similar to the liquid phase. Further heating leads eventually to a nucleated gas-phase transformation and ablation.

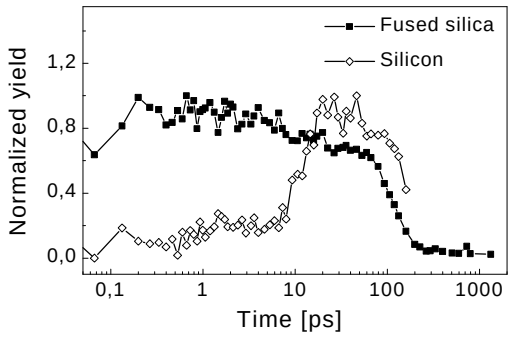

Fig. 2-2: Comparison between the fast Si^+ yield originating from a dielectric sample (fused silica) and a semiconductor (silicon) target.

Besides the intrinsic value of the time-resolved studies to obtain extended information on the mechanisms and ablation scales, there is an additional factor we were following in performing these experiments. The characteristic electronic response and the electron-lattice equilibration time can be exploited in irradiation with temporally shaped pulses. With emphasis on thermally-induced transformations, we have regarded how thermal effects can be guided to improve the structuring process rather than having a negative influence. An example will be given in the next chapter on the subject of ion acceleration using laser-induced transition to more absorptive phases.

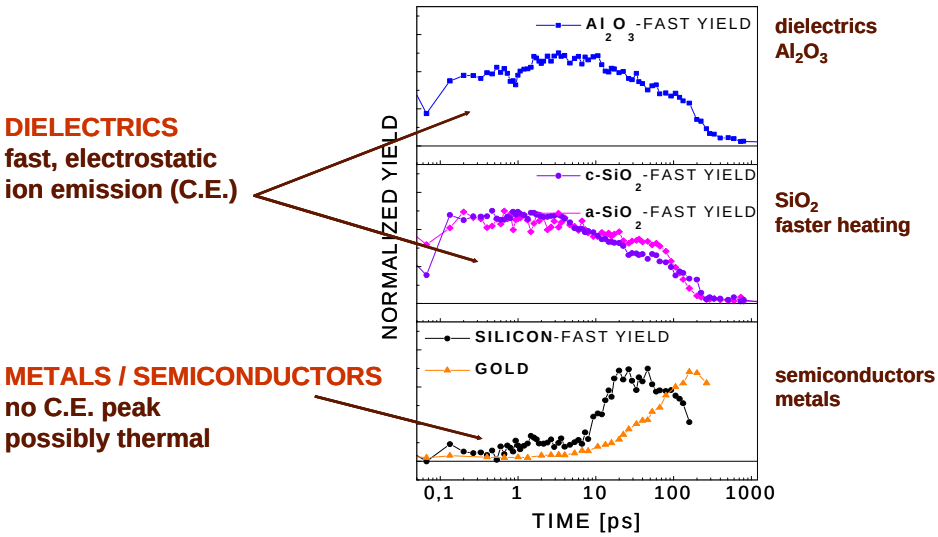

Fig. 2-3: Ion emission dynamics from irradiated materials with various electrical characteristics.

To obtain further information on phase transitions on non-transparent surfaces, we have additionally probed laser-induced solid to liquid transitions in silicon using a time-resolved reflectivity technique. The purpose was to elucidate the required melting time and transition to an absorptive liquid “metallic” phase for future control experiments. This dynamic confirmed also characteristic ablation times derived from light scattering

experiments from laser-disrupted surfaces [Sto00]. It is essentially the electron-phonon coupling strength that determines the major features and dynamics of the ablation process.

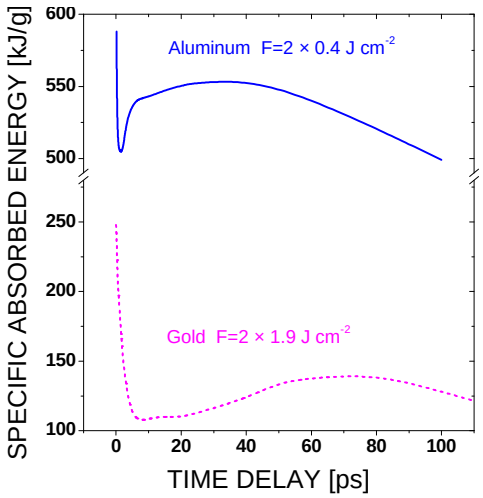

Fig. 2-4: Calculated specific energy density in gold and aluminum in double pulse experiments with sub-threshold intensities. The fast non-equilibrium excitation and the heating phase are visible.

In that concerns the response of metallic surfaces to laser irradiation, we have used the developed hydrodynamic model to perform numerical time-resolved experiments in order to determine the time correlation of optical and thermodynamic states. Interrogating optical properties can offer valuable information about coupled many-body interactions. Since this information comes in an embedded mode, the modeling approach was used to decipher the optical and the thermodynamic interplay. The model attempts to visualize the system evolution and to resolve in time the consequences of non-equilibrium electron heating on collisional rates, either electronic or electron-ion. This influence is consequently reflected on the optical properties (reflection and absorption) corresponding to the following phases of relaxation and expansion. Each thermodynamic state has a particular optical signature and determines a specific energy coupling efficiency either in the regimes of dense non-equilibrium matter or in the subsequent hot, expanding material. Fig. 2-4 shows an example of the accumulated energy density in gold and aluminum metals in double pulse exposure experiments with variable separation. The non-equilibrium electronic excitation, as well as the relaxation phases are visible and lead to the enhancement of energy deposition [CCS08-1].

2.2 Excitation channels in dielectric materials

In an ulterior attempt to identify major laser energy loss mechanisms, ultrafast laser excitation of dielectric materials was analyzed by monitoring the energy depletion of the excitation pulses (Fig. 2-5). The study was carried out within the diploma thesis of S. Winkler under my coordination and was trying to interrogated events during the laser pulse exposure, which influences the coupling of laser energy. The results indicated the energy balance in the

interaction process by observing in real-time the spatio-temporal variations of a laser pulse transversing a dielectric slab under its own self-actions. The optical observations allow insights into the development and the dynamics of the laser-induced free carrier population, emphasizing the role of the bulk effects related to the nonlinear wave propagation into the transparent material during laser exposure [WBH06-2].

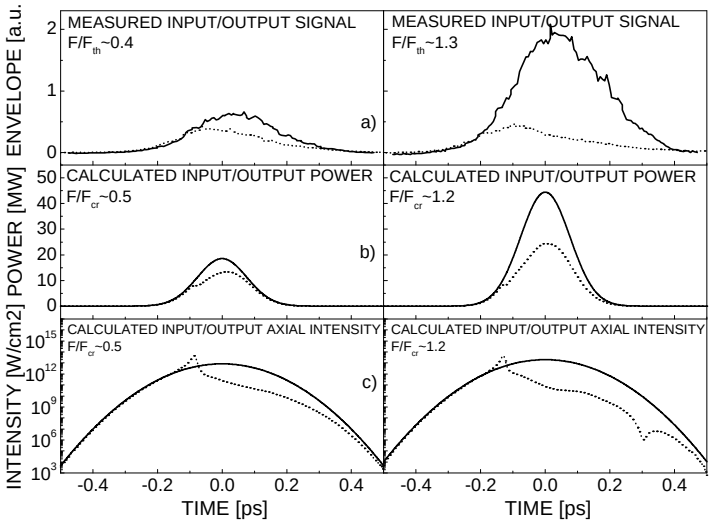

Fig. 2-5: Temporal envelopes of the pulses transmitted through the dielectric slab (dotted lines) at different input fluence values, below ($0.4\times F_{th}$) and above ($1.3\times F_{th}$) the surface damage level (F_{th}) for a 250 µm thick a-SiO_2 sample. The profile is measured after approximately 1 m of free-space propagation. The incident profiles are also depicted for comparison (solid lines).

The nonlinear propagation determines a secondary refocusing point inside the bulk, where, even in the absence of visible modifications, the region becomes absorptive, leading to the catastrophic collapse of subsequent pulses launched on a ps scale. This situation is depicted in Fig. 2-6, together with an estimation of single pulse-induced peak electron density in the second nonlinear focus. With increasing the input intensity, the nonlinear focus gradually moves to the position of the geometrical focus, located at the surface.

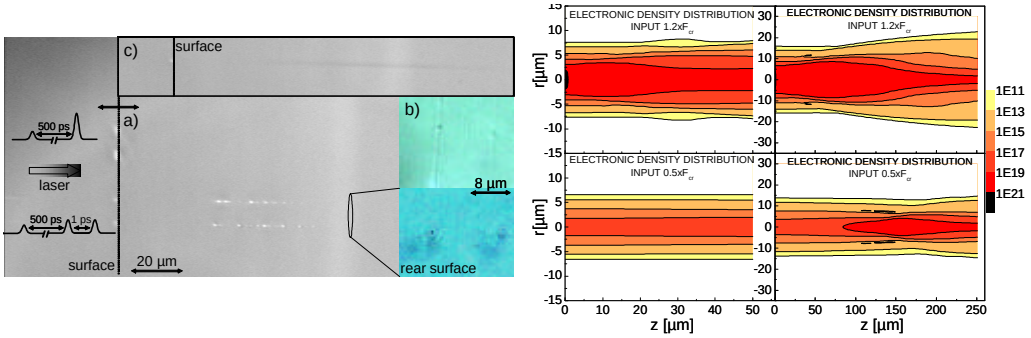

Fig. 2-6: Left: (a) Phase-contrast observations (side view) of bulk modification in fused silica samples excited with single ultrashort pulses and double pulse sequences focused on the surface. (b) Front view of rear side damage sites induced in thin samples (50 µm) by single pulse (top) and double pulse irradiation with 1 ps separation (bottom) at F=6 J/cm^2. In both cases the geometrical focus is located at the front surface. No rear damage appears after single pulse irradiation, while sub-diffraction-limited features can be identified for double pulse irradiation. (c) Coloration of the fused silica sample at repetitive single pulse exposure. Right: Numerical simulation on the laser-induced peak electronic density repartition [cm^{-3}] along the irradiated region for 50 µm (left) and 250 µm (right) thick a-SiO_2 samples.

2.3 Time-resolved refractive index changes in bulk transparent materials

To extend the time-resolved observations to the bulk of transparent materials, we have developed a particular microscopy technique. The dynamics of the formation of a phase object inside a dielectric material was observed using optical transmission and phase-contrast microscopy with sub-picosecond resolution. This was achieved by replacing the standard illumination path into a Zernike-type phase contrast microscope with a frequency doubled ultrafast beam (Fig. 2-7). Details about the experiment arrangement can be found in [Mer07].

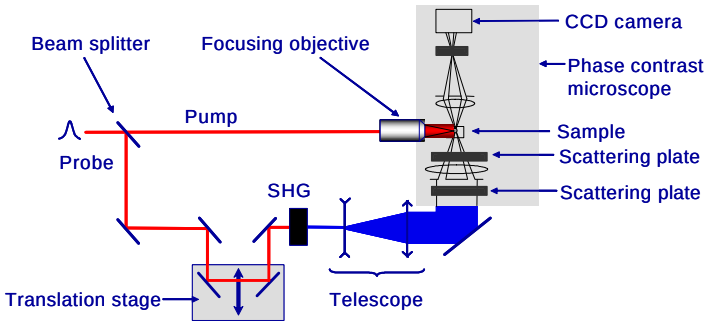

Fig. 2-7: Time-resolved phase-contrast microscopy for observation of the dielectric function.

We have concentrated on key question concerning excitation and the experimental approach allowed tracing the energy transfer from the initial energy deposition phase to the final structural relaxation. It also maps in time the complex dielectric function using the optical transmission (OTM) and phase-contrast (PCM) facilities. The setup permits insights into the decay of the laser-induced electron-hole plasma (Fig. 2-8) for various materials, and, at the same time, access into the behavior of the refractive index change (Fig. 2-9). Material evolution can thus be determined in different conditions of excitation.

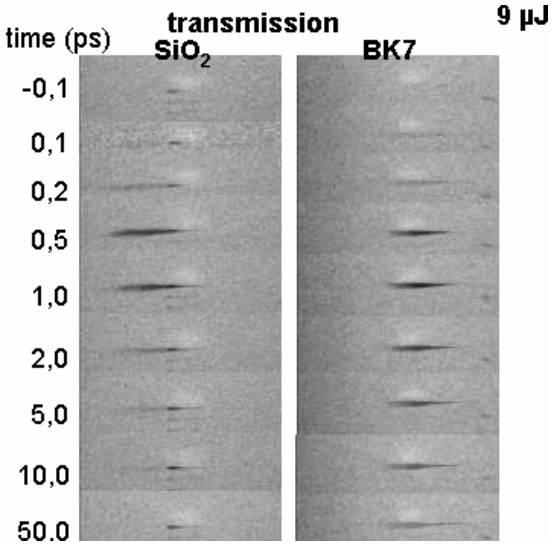

Fig. 2-8: Electron-hole plasma dynamics in fused silica and borosilicate crown BK7 visualized using time-resolved optical transmission microscopy (OTM). Different material characteristic relaxation rates can be observed; fast for fused silica and slower for BK7. Irradiation conditions: the input pulse energy is 9 µJ and pulse duration is 100 fs.

Various techniques were used so far to observe the excitation development [SJG05, HKP04, PZT07, BMS08], to interrogate the ionization efficiency, the dynamics of excitation, the collisional properties of the electron-hole plasmas, as well as the nonlinear propagation and shockwave generation. With a focus on the real and imaginary parts of the dielectric function, we have chosen the optical transmission and phase contrast microscopy techniques, combining high spatial and temporal resolution. The experiments were performed in collaboration with Max-Born Institute Berlin under the frame of a thesis in double supervision (A. Mermillod Blondin [Mer07]).

Plasma dynamics: Relaxation differences (Fig. 2-8) in several materials were indicated (e.g. fast relaxation in fused silica, slow electronic decay in BK7 (8 ps), or phosphate glasses) and correlated with specific thermodynamic and mechanical behaviors.

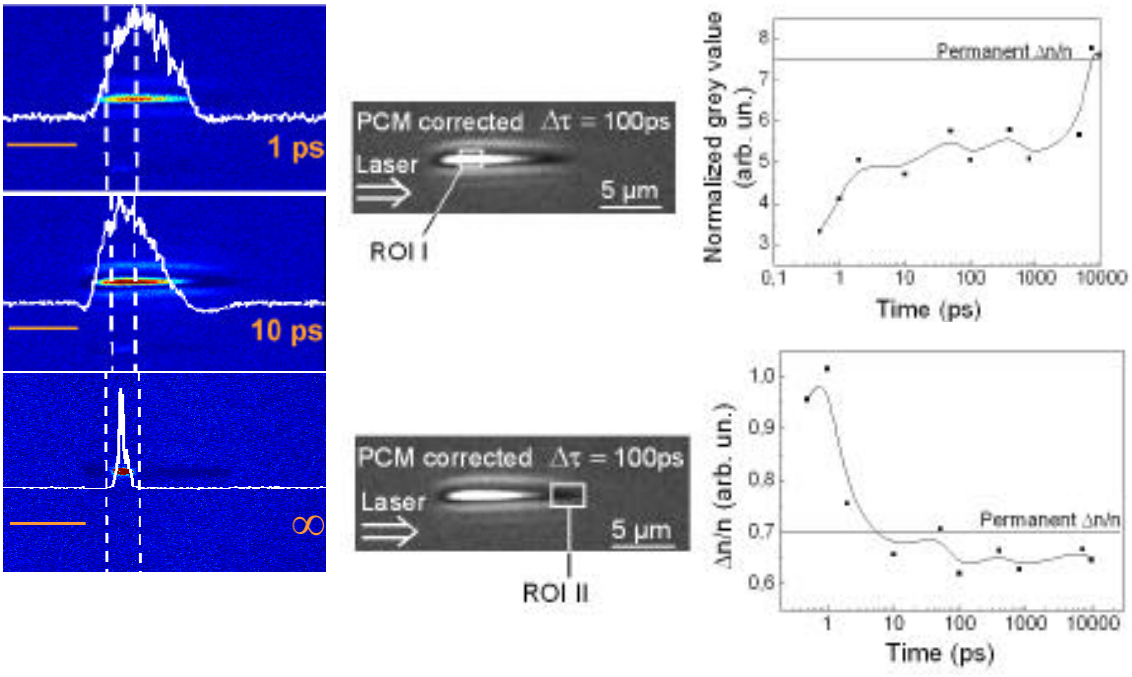

Fig. 2-9: Dynamics of refractive index changes in fused silica (time-resolved PCM microscopy). Irradiation conditions: the input pulse energy is 0.2 µJ and pulse duration is 100 fs.

Matrix dynamics: The behavior of different spatial regions with various refractive index variations was observed in the phase-contrast mode (Fig. 2-9), including regions of nonlinear concentration of energy. Visualizing the energy transfer to the glass matrix, a dynamic behavior on tens to hundreds of ps was subtracted for the formation of a micron-scaled void. This was found to be consistent with the launching of a shock wave due to fast heating and subsequent rarefaction at energies deposited in excess [ZXR04, STH07]. In the surroundings, fast compaction was noted, too fast to be explained by standard thermo-mechanical paths, suggesting that electronic effects may be at work. Specific emphasis was put on void formation due to its very small scale and the associated large index difference

from the surrounding, which indicates some interest in data storage applications [GM97] or in Bragg gratings for fiber optics [MAW06]. Organized arrays of nanoscale voids were recently reported under spatially-modulated laser excitations [KSH05] and were associated to steady state electron waves or to the presence of wavefront distortions. This material reordering occurs also at the nanoscale, together with a birefringent reorganization of matter due to plasmonic effects [SKQH03, BSC06].

A second point of interest concerns specific material characteristics. The mechanisms leading to the formation of a void indicate surrounding regions of high compaction, where structural transitions may occur. Recently, transitions to new phases was observed, which relates to the high temperature and pressure achieved in the void location [HBT06, HJM07], making these approach interesting for studying matter in extreme conditions [FiD86]

2.4 Summary

This chapter discussed relevant timescales for excitation, energy deposition, and material transformation paths. Material dependent effects in releasing the excitation energy either as electronic, vibrational enhancement, or swift lattice deformations were indicated. A balance and a time competition between electrostatic and thermal energy deposition were analyzed. The dynamics of laser-induced phase transitions was observed in non-transparent materials and discussed in a frame considering electronic correlation and diffusive transport of energy. Thermodynamic effects leading to density and refractive index variations were noted in the bulk of transparent materials upon laser irradiation. The extracted information allows predicting ablation scenarios, while delivering an extended basis for the interpretation of pulse-shaping experiments, advocating the possibility to implement design pulses. Thus, the excitation channels, the non-thermal and thermal relaxation paths, change the energy coupling dynamics, their balance being exploitable in laser control approaches which results in a “natural approach” to regulate both excitation and energy transfer towards optimal structuring. Understanding the underlying physics, the interrelation between processes can facilitate the optimization and determine an upgrade in quality for the laser-matter interaction process and the structuring results.

List of selected papers for presentation:

1) J. P. Colombier, P. Combis, E. Audouard, and R. Stoian “Transient optical response of ultrafast non-equilibrium excited metals: Evidence of an electron-electron contribution to collisional absorption” Phys. Rev. E 77 036409 (2008)

2) S. W. Winkler, I. M. Burakov, R. Stoian, N. M. Bulgakova, A. Husakou, A. Mermillod-Blondin, A. Rosenfeld, D. Ashkenasi, and I.V. Hertel “Transient response of dielectric materials exposed to ultrafast laser irradiation” Appl. Phys. A 84, 413 (2006)

3) D. Ashkenasi, G. Müller, A. Rosenfeld, R. Stoian, I.V. Hertel, N. M. Bulgakova, and E.E.B. Campbell “Fundamentals and advantages of ultrafast micro structuring of transparent materials” Appl. Phys. A 77, 223 (2003)

4) R. Stoian, A. Rosenfeld, D. Ashkenasi, I.V. Hertel, N.M. Bulgakova, and E.E.B. Campbell “Surface charging and impulsive ion ejection during ultrashort pulsed laser ablation” Phys. Rev. Lett. 88, 097603 (2002)

5) I.V. Hertel, R. Stoian, A. Rosenfeld, D. Ashkenasi, and E.E.B. Campbell “On the physics of material processing with femtosecond lasers” Riken Review 32, 23-30 (2001)

6) R. Stoian, D. Ashkenasi, A. Rosenfeld, M. Witmann, R. Kelly, and E.E.B. Campbell “The dynamics of Ion Expulsion in Ultrashort Pulse Laser Sputtering of Al_2O_3” Nucl. Instrum. Meth. B 166-167, 682 (2000)

Chapter 3: Creating light-matter synergies

It was mentioned before that among the various properties of ultrashort laser pulses that are attractive for material processing, there is one factor which is often claim as a dominant characteristic of ultrafast interaction: diminished thermal effects and the subsequent reduced heat-affected-zones. The question we asked ourselves in this context was related to the possibility to use heat as a beneficial factor for processing applications. Extending the concept, we have searched the perspective of influencing material reactions using light that self-modulates according to these transients. In this perspective, exploiting the spectral and spatial coherence of the laser pulse, we have developed a beam manipulation technique able to control thermal or other material effects towards improving the structuring process.

3.1 Spatio-temporal pulse shaping

The newly developed techniques of spectral and spatial phase modulation have allowed flexible programmable beam spatio-temporal shaping [Wei00]. Specifically, temporal pulse shaping by complex Fourier synthesis of frequency components has been demonstrated to be an effective technique able to regulate a variety of physical and chemical systems and to route specific processes in pre-specified directions [MS98, ABG98]. Complex electromagnetic waveforms can be generated using the laser pulse spectral characteristics, with the potential to manipulate the interaction between light and matter.

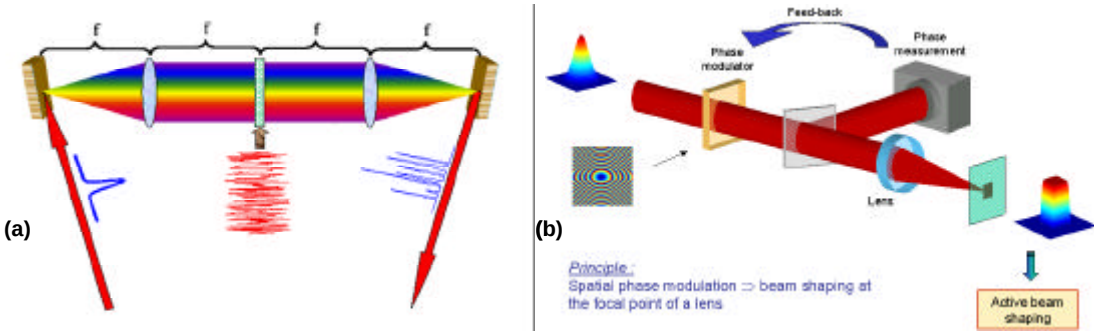

Fig. 3-1: Schematic representation of the temporal (a) and spatial (b) pulse shaping concepts.

Widely used in femtochemistry for control of molecular dissociation, selective bond breaking, or charge transfer in biochemical complexes, tailored pulses can show benefits for material processing, as similar molecular processes occur at macroscopic scales. We have therefore initiated a program for testing the potential of temporal pulse shaping in ultrafast laser material processing. Similar beam engineering concepts can be used for spatial phase modulation, leading to arbitrary profiles for the laser intensity (Fig. 3-1) [SHL05].

3.2 Experiments with tailored pulses

Preliminary experiments initiated at the MBI during my postdoctoral stay have shown a significant improvement in the quality of the induced structures using temporally shaped pulse trains with sub-ps separation [SBC02-5, SBH03-4, SKH03-3]. A situation where reduced exfoliation is displayed by structures induced in CaF_2 irradiated by modulated pulses is presented in Fig. 3-2. The improvements can be related to a transient change in the material properties as a consequence of swift excitation and relatively strong electron-phonon coupling and charge trapping. The sequential energy delivery induces a preparation of the surface (i.e. defined electron density, phonon temperature, and lattice deformations) and an associated material softening during the initial steps of excitation, thus changing the energy coupling for the subsequent steps. This leads to lower stress, cleaner structures, and provides a material-dependent optimization process. Especially for brittle material with strong electron-phonon coupling, carrier self-trapping, lattice-induced deformations, softening, and controlled heating can be advantageous since they provide the means for relaxation of the induced stress, with a reduction of macroscopic cracking and fracture phenomena. This is also consistent with previous demonstration of burst micromachining using multipeak sequences on MHz scales [HLB00]. Potential applications may be envisaged in soft processing and optical polishing.

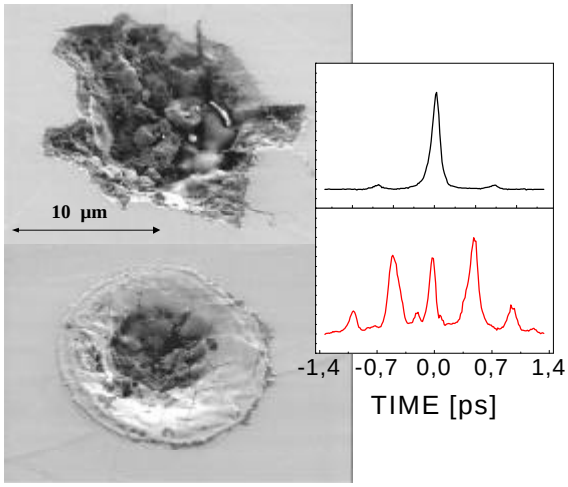

Fig. 3-2: Reduced exfoliation in brittle materials (CaF_2) by irradiation with laser pulse trains modulated on THz scales. Structures made on CaF_2 with single pulse (upper part) and triple-pulse sequences (bottom part) at repetitive irradiation per site (N=5). The fluences are increased for the triple-pulse irradiation to simulate comparable conditions for removal efficiency. The images correspond to 7 J/cm^2 respectively 12 J/cm^2. The initial pulse duration is 90 fs. Right: corresponding irradiation sequences.

Furthermore, multiple pulse sequences were used to control the occurrence of optical damage, the profile, and the characteristic size of the induced structures in various dielectrics (a-SiO_2, Al_2O_3), leading to a change in the ablation morphology [SBH03-4, SBC02-5]. For fused silica, the temporal control on the spatial crater profile and morphology patterns is

facilitated by the temporal synchronization with the electron trapping dynamics. The spatio-temporal coupling provided by the material nonlinearities allows the possibility to design spatial excitation features which map in space the temporal modulation of the laser pulse. Improvements were observed as well for deep drilling of channels in fused silica samples using multipulse sequences on THz scales.

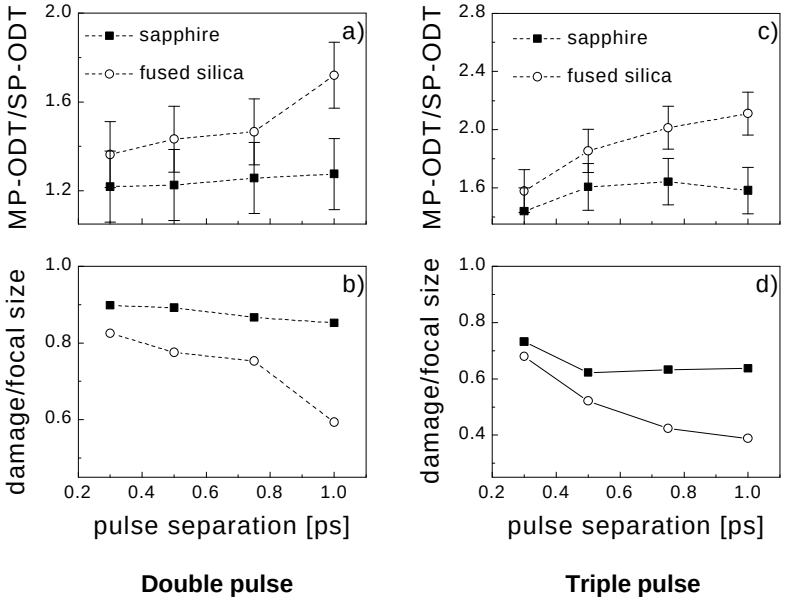

Fig. 3-2: (a, c) Optical damage thresholds for Al_2O_3 and a-SiO_2 for double and triple-pulse irradiation (MP-ODT, considering the total energy of the sequence) relative to the single pulse damage (SP-ODT) at different pulse separation times. (b, d) Multi-pulse damage dimensions relative to the focal spot for Al_2O_3 and a-SiO_2 for different pulse separation times and fixed fluence. Smaller structures are obtained when pulse trains are used.

A 2-D simulation model for optical breakdown under the action of temporally shaped laser radiation was developed together with I. Burakov and N. Bulgakova to study the dynamics and the subsequent spatial modulation of electronic excitation and heating in materials with various coupling strengths [BBH05-2]. The model sheds additional light onto the characteristics of optical dielectric breakdown, taking into account the temporal and spatial evolution of the free-electron density, defect accumulation, the energies of electron and lattice subsystems, and the optical response in the dielectric targets under the action of temporally modulated pulse intensity envelopes. Modeling was performed for sapphire and fused silica in order to emphasize the material-dependent energy-deposition time scales as specific domains for tailored pulses (modulated electronic excitation and optimal energy transfer to the lattice) for particular experimental conditions. The temperature profiles obtained by modeling were analyzed and compared with the experimental data on crater shapes and dimensions. It has been found that the development of spatially modulated optical properties related to fast plasma evolution is responsible for the formation of the modulated crater in fused silica.

For semiconductor samples improvements were seen in the structuring quality by using multipulse sequences [SKH03-3]. Synchronizing the laser temporal irradiation profile with the solid-to-liquid phase transition time and the associated augmentation in the absorption efficiency, conditions can be found to evaporate the resultant liquid layer and to avoid its gradual cooling and return to the surface as recast. Fig. 3-3 shows an example were single short pulse sequences generate thick liquid layer and an increase in hydrodynamic activity with respect to visibly cleaner structures induced by multipulse peaks, supporting thus a scenario of total vaporization of the melted front.

As a natural follow-up, in recent experiments evolutionary algorithms using nature-mimetic approaches and spatio-temporal pulse tailoring as a functional degree of freedom have been implemented for material processing. Examples on adaptive optimization results will be treated in the next chapter.

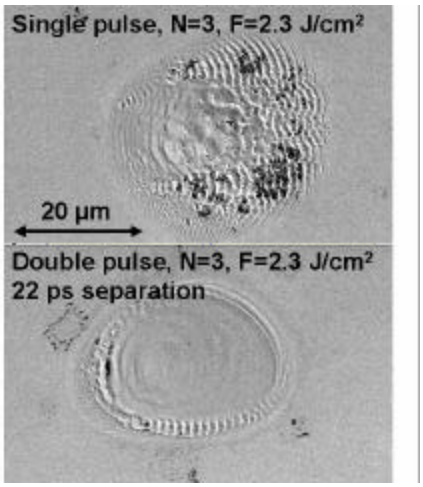

Fig. 3-3: Surface structures generated by laser ablation of silicon with short pulses (180 fs) and multipulse sequences. The topographical aspect indicates a change in the energy coupling properties. While the single-peak irradiation generates significant melt residuals that suggest strong thermal and hydrodynamic activity, double-pulse irradiation produces clean structures by efficiently coupling the second pulse into the initially induced liquid region. The irradiation conditions are indicated on the figure.

At the same time, following a collaboration with the group of diffractive optical elements (O. Parriaux, D. Pietroy - LabHC), efforts have taken place to develop compact (monolithic) beam shaping devices for simpler pulse forms using spectral resonances on resonant gratings [PFQ08-1]. Since the quality of processing can be improved by designing modulated pulses on the timescale of electron-phonon coupling, the effort is justified by the attempts to facilitate the insertion of beam shaping devices in industrial practice.

3.3 Summary

These experiments have underlined the importance of a detailed know-how of the ultrafast laser interaction. Knowledge of the response times of materials establishes a

guideline for using spatio-temporally tailored pulses in order to optimize the structuring process with respect to the efficiency of material removal, the quality of the appearance, and reduction of the residual damage. Correlations with the charge trapping and defect production timescales or with relevant dynamics of structural phase transitions were indicated. The observations described above demonstrate that in order to achieve progress in the possibility of influencing material modification on surfaces, sub-surface, and bulk regions, it is of paramount importance to promote knowledge concerning temporal behavior of the:

- energy absorption and dissipation
- the dynamics of carrier generation, transport, localization and heat deposition in the phonon modes, together with the formation and accumulation of defect centers
- changing in a predictable and reproducible way the properties of the material.

Employing THz repetition rates (~sub-ps time scales) and advanced pulse manipulation methods enabled us to believe that controlled processing is possible, based on the synchronization between the excitation sequence and the individual electronic and lattice ps response of the material.

List of selected papers for presentation:

1) D. Pietroy, M. Flury, O. Parriaux, C. Liebig, R. Stoian, and E. Quesnel “Ultrashort pulse splitting upon resonant reflection on a mirror-based waveguide grating” Opt. Express accepted (2008)
2) I. M. Burakov, N. M. Bulgakova, R. Stoian, A. Rosenfeld, I.V. Hertel “Theoretical study of the possibility of material modification with temporally shaped femtosecond pulses” Appl. Phys. A 81 1639 (2005)
3) M. Spyridaki, E. Koudoumas, P. Tzanetakis, and C. Fotakis, R. Stoian, A. Rosenfeld, and I.V. Hertel “Temporal pulse manipulation and ion generation in ultrafast laser ablation of silicon” Appl. Phys. Lett. 83, 1474 (2003)
4) R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, and I.V. Hertel “Dynamic temporal pulse shaping in advanced ultrafast material processing” Appl. Phys. A 77, 265 (2003)
5) R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, I.V. Hertel, and E.E.B. Campbell “Laser ablation of dielectrics with temporally shaped femtosecond pulses” Appl. Phys. Lett. 80, 353 (2002)

6) R. Stoian, M. Boyle, A. Thoss, A. Rosenfeld, G. Korn, and I.V. Hertel “Ultrafast laser material processing using temporal pulse shaping” Riken Review 50, 71 (2003)

7) E. Koudoumas, M. Spyridaki, R. Stoian, A. Rosenfeld, P. Tzanetakis, I.V. Hertel, and C. Fotakis “Influence of pulse temporal manipulation on the properties of ablated Si ion beams” Thin Solid Films 453-454, 372 (2003)

Chapter 4: Self-learning irradiation tools

We have indicated so far that achieving control on matter transformation by energetic beams has beneficial consequences for material processing. Smart processing techniques may be developed; meaning the ability to self-modulate, accommodate transient variations in the irradiation conditions, and respond to a maximum of user demands. However, if only to resume some of the conclusions of the previous chapters, material modification or ablation is a consequence of energy coupling, which becomes here the main observation object. Among the issues that will be discussed, we focus on transient changes of material properties and the possibility to take advantage of them for optimal coupling. The coupling efficiency can be changed by transforming material optical properties via the electronic contributions to the dielectric function or by the temperature dependence of electronic collisional rates. Additionally, a controlled balance between energy input and losses can be established, including the selected thermodynamic path for the excited material. The interaction character can be regulated not by a brute force but by optimally synchronizing the laser radiation to the transformation sequence. We have previously seen the potential of temporally shaped pulses to influence light-induced processes and we have anticipated the possibility that optimally tailored laser pulses can be derived. The mutual assistance between light and matter can be adaptively mastered using control feedback loops based on programmable pulse shaping. This implies the automated modulation of light so that it becomes capable to guide transient phase transitions and structural modification, to regulate the heat flow, and, in turn, to exert a positive influence on the irradiation process. Light will react to individual material responses, becoming thus a matter-adaptable tool which can than be integrated in adaptive loops. An example of a control loop is given in Fig. 4-1, emphasizing the general requirements; a pulse control unit and a way to quantitatively evaluate the laser action (here, a time-of-flight mass spectrometry unit to record the particle ejection yield). If the interaction has an intrinsic complex character, self-learning optimization algorithms driving the control loop can supplement the lack of information concerning the physical mechanisms of interaction, providing as well insights into the control factors driving the system in designed states.

Following the information derived in the previous parts concerning various mechanisms and interaction dynamics, this chapter puts forward several directions of research including the prospect of controlling the thermodynamics of the interaction process or designing phase-space trajectories, and, as well, the possibility to optimally structure the bulk of transparent materials. It also involves the technical setup of the loop, detection of laser

effects via spectroscopy and microscopy, and the development of control algorithms (pulse forming algorithms, evolutionary strategies, simulated annealing, Gerchberg Saxton approaches). These approaches were developed under my coordination in several undergraduate and graduate works [Mer04, Mer07, Mau07].

4.1 Energy coupling at non-transparent interfaces. Controlling phase transitions and thermodynamic trajectories

High level of electronic excitation in solid materials triggers lattice instabilities and, consequently, mechanical and thermal alterations of the material structure. The modified regions carry novel mechanical, electrical, and optical characteristics. These structural or thermodynamic phase transitions occur on fast scales and a certain control of their competition may be established, which leads to the creation of metastable properties around critical points or transitions to potential energy states hardly attainable by other means. These effects are important for surface treatment and patterning or in applications related to optical switching or forward transfer [SAM94, KLC08]. In recent experiments, evolutionary algorithms were implemented for material processing. Several examples describe issues related to energy coupling, conversion, non-equilibrium phases, and particle emission.

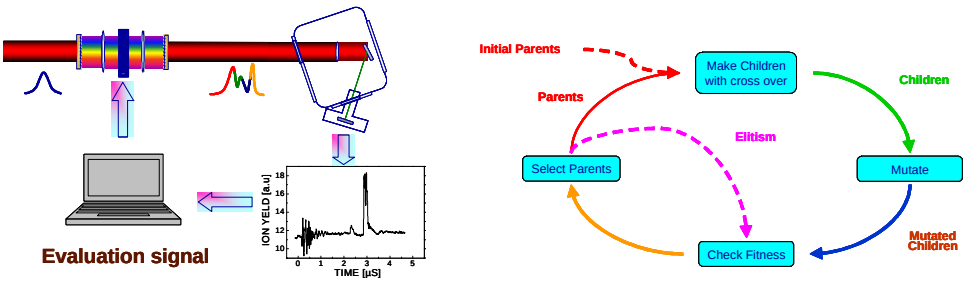

Fig. 4-1: Left: Adaptive loop developed for the optimization of the ion yield based on a time-of-flight mass spectrometer. Right: Basic description of an adaptive optimization strategy involving iterative application of genetic propagators to control the search space.

a) Kinetic acceleration of laser ablated ions: Acceleration and kinetic tunability of ions was observed during laser irradiation of silicon on ps scale. The approach has illustrated a versatile possibility to optimize the kinetic properties of the Si^+ ions emitted from laser irradiated semiconductor samples by taking advantage of a fast succession of structural transitions. This was accomplished involving excitation sequences synchronized with the phase transformation characteristic times (Fig. 4-2). The optimal irradiation sequence was obtained using an ion-detection based optimization loop guided by an adaptive strategy and is represented by a fast peak followed by a ps tail of energy distribution. The acceleration mechanism was connected to an improved energy coupling related to the formation of a transient highly absorptive liquid Si state initially triggered by fast single and two photon

absorption.. For comparison, the absorptivity in the crystalline phase at 800 nm is mainly determined by single and two photon absorption events, being considerably reduced with respect to the excited state with metallic character.

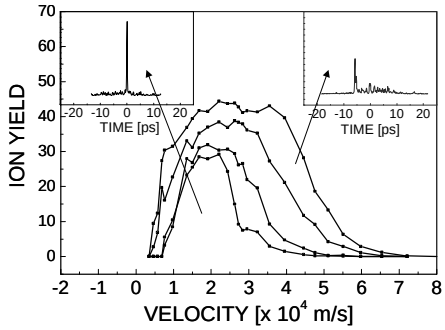

Fig. 4-2: Energetically tunable Si^+ ion beams generated by laser ablation of silicon with ultrashort and adaptively generated temporal pulse shapes. Irradiation conditions: initial pulse duration 170 fs, input fluence 0.8 J/cm^2.

The analysis of the optimal pulse shape allows to predict the following scenario. The first pulse in the sequence determines a thermal solid-to-liquid transformation, while the tail of the irradiation sequence couples very efficiently to the molten layer. The higher absorptivity (1000x) and the lower electronic mobility determine significantly higher temperatures, above the critical point, leading to the sudden decomposition of the excited material. This generates highly energetic and volatile thermodynamic paths with minimal energy expenses, making accessible thermodynamic states around the critical transition points [SBH05]. Short pulses induce lower temperatures indicating that phase transformation occurs via homogeneous nucleation [PLM03].

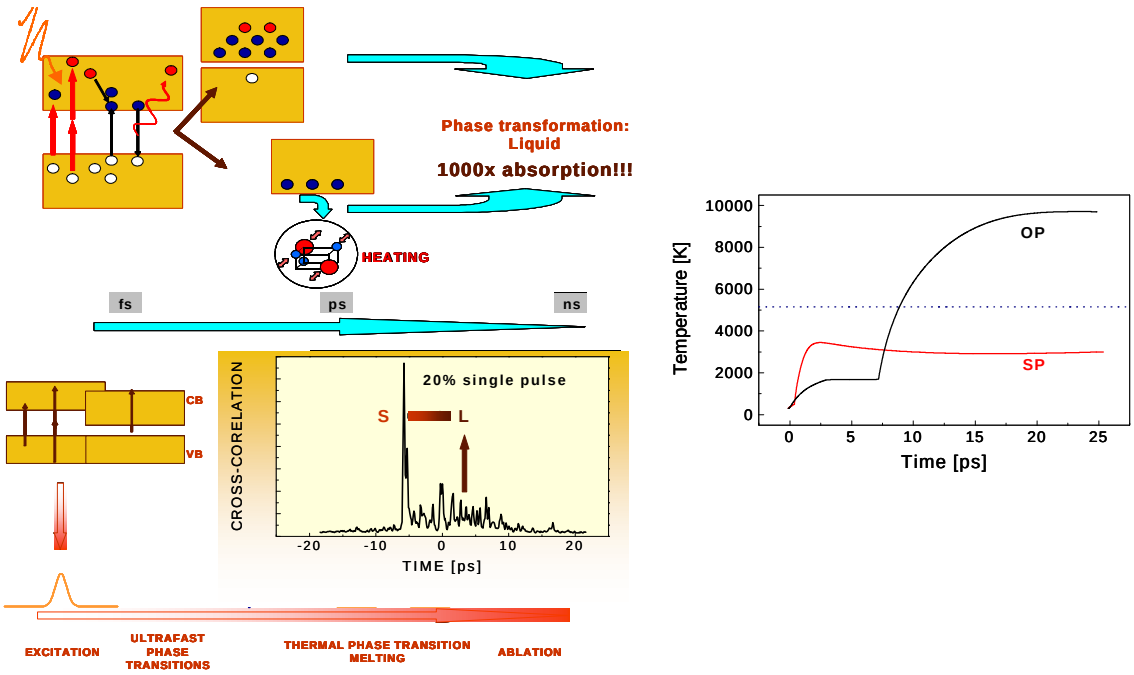

Fig. 4-3: Concept of absorption, thermalization and formation of a laser-induced phase transformation in silicon, together with the temperature variation. Enhanced energy coupling into the melt pool can lead to overheating. Irradiation conditions are similar to Fig. 4-2.

Control of kinetic and directionality properties of laser-induced ion beams carry a fundament character, nevertheless, these characteristics are key factors for low energy shallow implantation profiles in ion implantation techniques. This particular aspect was performed together with the Institute for Electronic Structure and Laser at FORTH, Heraklion.

A schematic representation of the succession of laser-induced phase transformations is given in Fig. 4-3, indicating the main absorption mechanisms in the solid phase together with the absorption enhancement in the liquid phase, derived from the action of the optimal pulse. A thermal model was developed to characterize the temperature increase which showed the energy localization into the melt pool as the reason for the energetic ion emission.

b) Structural transitions: More recently, a research direction was established concerning adaptive solid-to-solid structural transitions in covalent polymorphic materials with high electronic correlation, due to potential structural transformation induced by electronic excitation [SAM94, WBL05, WY07, WBW07]. The work was performed during the postdoc stay of C. Liebig.

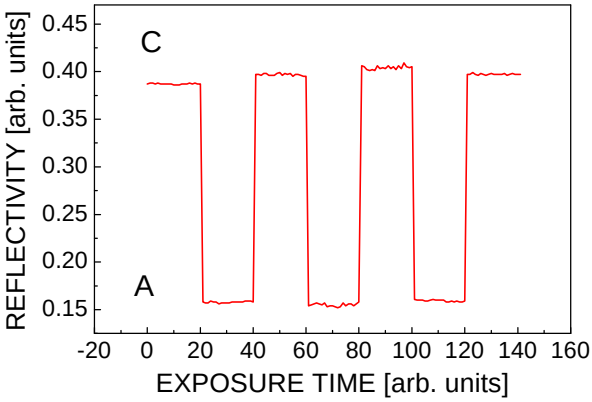

Fig. 4-4: Alternate reflectivity variations as the structure changes from crystalline (C) to amorphous (A) phases in DVD-like phase change materials under the action of long (ps) respectively short (fs) laser pulses close to the material melting threshold.

The project was focused on reversible amorphous-to-crystalline phase transitions in phase change materials based on GeSb alloys, generated by variable pulse shapes. High reflectivity crystalline phase are generated by picosecond long irradiation of amorphous surfaces, while the reversed transition to the amorphous phase was realized by ultrashort pulses. Reversible amorphous to crystalline phase transitions were shown to be controllable using the pulse form, leading to a subsequent modification of the sample reflectivity (Fig. 4-4). The crystallization efficiency via the formation of a high density of nuclei depends on the laser-induced temperature gradient into the sample and the lifetime of the liquid phase, which can be modulated by variable energy coupling. The interest resides in the strong variation of optical properties associated with these materials with potential in data storage applications.

c) Linear materials: If for a low band-gap material (see the above examples) the main factor of improving energy deposition is related to a fast change to an absorptive state, other materials show no significant differences in the dielectric function between the solid and the liquid phase at the photon energy of 1.5 eV and, therefore, no absorption enhancement. This is the case of metallic aluminum. The relevant question is then related to the factors that may improve the energy coupling in this case. Commonly for metals, electronic excitation determines a high temperature, high pressure phase, and, presumably, the evolution control factors involve hydrodynamic advance. This has consequences on the transient optical properties, and, equally important, on the heat transport characteristics. Feedback-based ion emission was used as a probe of the efficiency of energy deposition into the material. Ion acceleration effect was observed, similar to the Si case, and explained by a laser pulse regulated balance between the mechanical and thermal energy of the ablation products, due to the fast hydrodynamic movement of the excited material and the associated density variations. If ultrafast radiation, as it will be explained below, favors the accumulation of mechanical energy in the ablation products due to a fast pressure release, the picosecond tailored envelope determines a preferential heating of the ablation products, which induces variations in the ionization degree, while still keeping the losses by heat conduction at a minimal level This constitutes a first example of controlling thermal effects and designing thermodynamic trajectories to achieve control of the interaction process and has consequences for the processing accuracy or composition of ablation products, or for other quality criteria such ablation efficiency, smoothness, or aspect ratios. On the other hand, it constitutes a description of thermal manipulation for interactions longly considered as athermal.

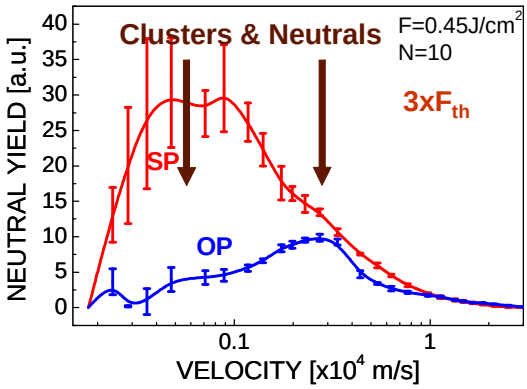

Fig. 4-5: Velocity distributions of ablation products (neutrals and clusters) generated under ultrafast and optimally-tailored laser irradiation of aluminum. A decrease in nanoparticle production is observed for optimal excitation (together with ion acceleration-not shown).

d) Control of nanoparticle production: In parallel to ion acceleration, a strong decrease in nanoparticle emission was observed from metallic targets irradiated with temporally shaped laser radiation. The effect is illustrated in Fig. 4-5 for Al irradiated with

ultrashort and optimal pulses. Ultrafast irradiation is associated with an initial isochoric increase of pressure due to electronic excitation. The pressure release determines a fast expansion across the binodal and the ejection of nanodroplets from the liquid phase inserted a vapor-liquid droplet mixture. The thermodynamic conditions of evolution for the ablation plasma and, essentially, the passage in the vicinity of the critical point, additionally determine the efficiency of matter recondensation in form of nanoparticles. The tailored pulse favors instead the heating of the expanding material and determines a dominant transition to a gas phase with low particulates content [CCS06].

e) Dynamics of excited materials and simulation of energy coupling: A hydrodynamic code based on a Lagrangean formalism was developed and applied to study materials behavior under laser excitation on ultrafast scales. As mentioned in Chapter 1, this development benefited from the participation of J. P. Colombier, lecturer at the Jean Monnet University. The approach, which has at the base a source developed at the Commissariat a l'Energie Atomique (P. Combis, CEA) is well suited to predict complex thermodynamic and thermo-mechanic trajectories. With the simulation support we have analyzed the consequences of energy coupling for the subsequent material transformation phases. The sequential energy transformation into mechanical and thermal forms creates the premises of particular phase transformations and, despite the reduced sensitivity for intensity dependent effects for linear materials, the overall absorption efficiency can be elevated if the proper conditions for density and temperature are met for the expanding layers.

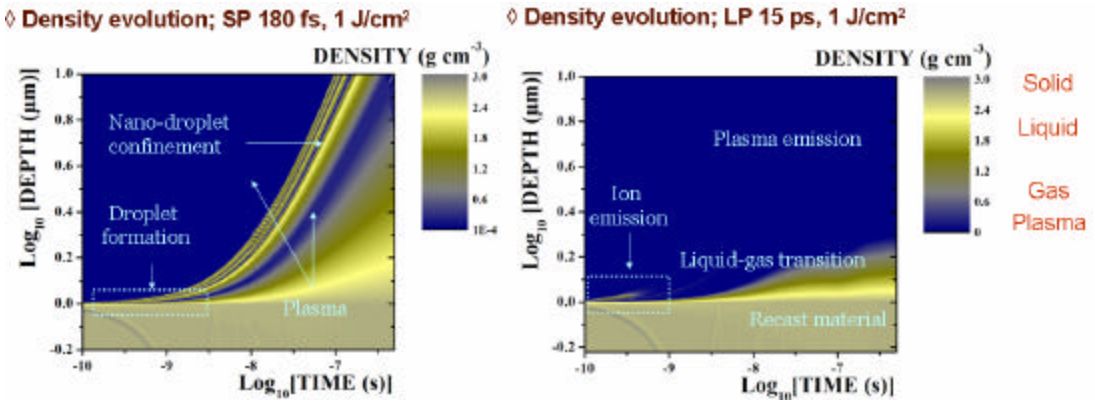

Fig. 4-6: Material ejection under laser excitation of aluminum for short (left) and optimal (right) pulses. Calculation of transient density phases. The onset of liquid nanolayers is observable for ultrashort pulses. The liquid layers expand under confinement between gas layers. Optimal pulses generate a preferential transition to the gas phase.

Thermodynamic trajectories leading to nanoparticle formation were equally analyzed. For example, as seen the previous paragraph, nanoparticle ejection was indicated under the form of nanoscale liquid layers for short pulse irradiation. The density diagram of the ablation flow is given in Fig. 4-6, presenting the case of laser irradiated Al. The hydrodynamic model

was further developed to take into consideration dynamic evolution of optical properties of laser excited materials. The approach validates the transition from a solid material to plasma regimes, while emphasizing the role of the umklapp electron-electron collisions in promoting higher absorption in the initial crystalline phase, assuming as well a variation of electronic momentum. This allows insights into the energy deposition and has consequences for understanding the dynamics of laser-induced transitions.

f) Liquid trapping: Under fs laser excitation, following the isochoric heating and due to a competition of mechanical and thermal energy relaxation channels, some of the expanding layers have a fast passage across the binodal. This is particularly due to the transformation of potential electronic energy in mechanical expansion energy. In between, liquid is trapped and localized at the liquid-gas interface (Fig. 4-7), and its subsequent evolution determines the apparition of nano-droplets which expand under gas-confinement (Fig. 4-6). The trapping time is significantly reduced when using temporally shaped radiation, with consequences for the probability of droplet ejection from the liquid phase. The softer heating process leads to a significant superheating of the superficial layers and specifically favors a gas-phase transformation. The formed liquid does not have enough energy to expand and returns to the solid phase as recast. This aspect has consequences for the rate, shape, and the dimensions of the produced nanoparticles. Premises are created for optical tunability via nanoparticle size-control and consequences for nano-fabrication, breakdown spectroscopy, and pulsed laser deposition are analyzed.

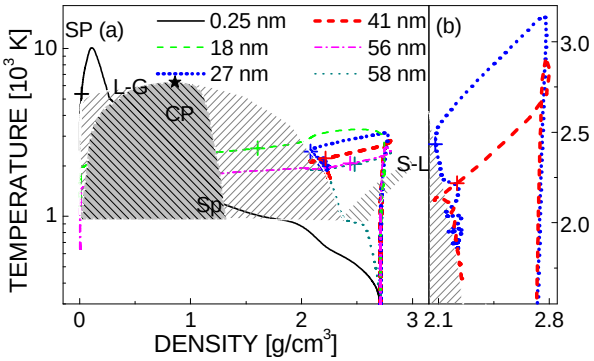

Fig. 4-7: (a) Thermodynamic trajectories of different material layers under ultrafast laser excitation of Al indicating the initial isochoric excitation and the passage to the mixed phase region. (b) blow up the binodal intersection indicating the trapping of low density material at the liquid-gas interface (binodal-shaded region). The input fluence (1 J/cm^2) is approximately twice the calculated ablation threshold.

This discussion has indicated several factors defining the laser energy coupling efficiency, the regulator factor of electronic collisions via temperature in conditions of electron-ion nonequilibrium, the deriving transient optical properties, heat transport, and energy conversion factors. These factors and the subsequent thermodynamic behavior can be

mastered using controlled energy feedthrough and are prerequisites for tailoring the optical absorption as well as the laser ablation outcome, structure, and plume kinetics.

4.2 Adaptive optimization of refractive index changes in the temporal domain

In that concerns transparent materials, the ability to design the dielectric function on minimal scales is based on the potential balance of electronic and structural transformations associated with the refractive index change. The local modification is an interplay of several factors, including generation of defects, modifying the local dielectric structure, or accumulating stress. Their relative importance can assist in engineering particular index changes. This can be achieved by a judicious synchronization and mutual assistance between irradiation and matter evolution, in the condition where the transformation sequence is jointly determined by the material response and the spatio-temporal character of excitation [BBH07].

We developed an advanced material structuring approach based on adaptive pulse spatio-temporal manipulation for optimizing ultrafast laser-induced processes inside transparent materials (Fig. 4-8). In this approach, the pulse control unit and the laser action microscopy evaluation unit are coupled together via a closed feedback loop, guided by a global optimization strategy in the spatio-temporal domain. Due to the complexity of the laser-matter interaction process, self-learning algorithms based on a spectral/spatial parametrized search space and using nature-mimetic approaches are used to control and guide the loop. The main objective is the photoinscription of light waveguiding objects. We will follow below two main strategies for influencing the material transformation under light exposure, adaptive temporal tailoring techniques and spatial beam forming.

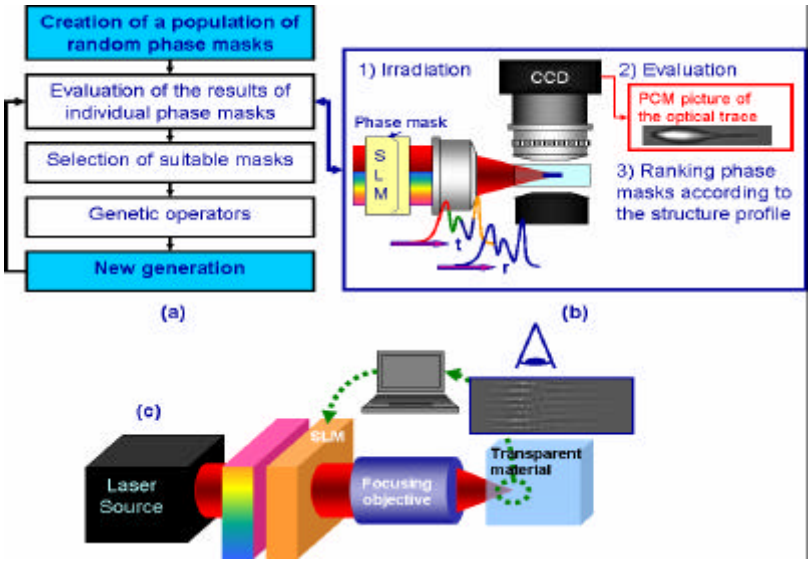

Fig. 4-8: (a) Main steps of the optimization procedure; evaluation of the phase masks (spectral or spatial) and generation of new solutions. (b) Blow-up of the phase-pattern evaluation sub-steps: irradiation of the sample with the phase mask, estimation of the corresponding trace profile, ranking of the phase mask. (c) The adaptive spatio-temporal feedback loop.

From a general perspective, the material response to optical excitation is determined by the relaxation properties of the glass and the extrapolation of photoinscription techniques should take this into account, as well as possible means to determine a suitable material behavior. During the waveguide photoinscription process we noted a very important role of the material properties and of the propagation characteristics in the resultant refractive index change. The irradiation outcome determines a complex dielectric design and electronic and structural alterations associated with either increasing or decreasing the refractive index under light exposure. In many glassy materials the standard ultrafast radiation induces merely a decrease of the refractive index, detrimental for waveguiding. Speculatively, this is related to a high dilatation coefficient triggering volumetric expansion. Guiding regions may be restricted to stressed region around the excitation area. The possibility to reverse the natural tendency to rarefaction towards compaction carries a strong fundamental and technological significance. The follow-up idea is to design a type of irradiation able to overturn the standard material response towards a prior established user request, for example producing positive refractive index changes in materials were the regular response is rarefaction. The temporal beam modulation techniques are natural candidates for this task due to their influence on the physical behavior of the interaction process. In this perspective, dynamic control over the energy delivery leads to an upgrade in the quality of the laser-induced structures and enables precise refractive index engineering. The technique allows to detect and influence dynamical processes on molecular and mesoscopic scale in a controllable manner towards a non-standard user-defined output. The laser energy delivery rate adjusts itself adaptively to control transient phenomena and to match best coupling conditions.

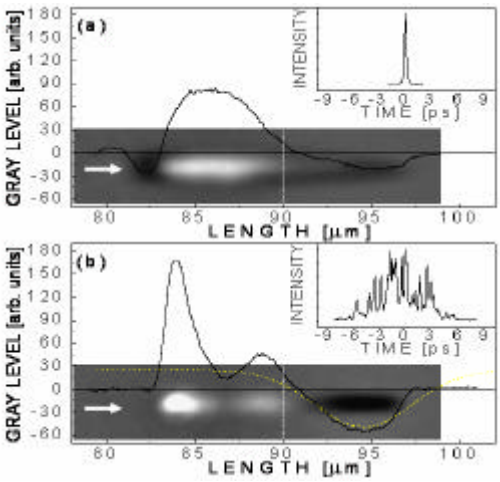

Fig. 4-9: Refractive index flip in borosilicate crown BK7 under short and optimally tailored irradiation. Phase contrast microscopy images of refractive index changes (white colors represent negative refractive index changes, black colors represent positive refractive index changes). The result of standard ultrafast irradiation 150 fs (top) and optimized 4.5 ps excitation (bottom) are indicated. The onset of a significant compression zone is becoming visible under optimal conditions. Pulse energy 0.17 μJ, irradiation dose 10^5 pulses.

Experimental development: We have accomplished the realization of a "real-time" phase contrast microscopy setup which can deliver time-resolved refractive index observation with sub-picosecond resolution. The microscope is integrated with a spatio-temporal shaping unit (which performs the functional variation of the space and time envelope) and provides the quantitative evaluation of the laser action. Thus, "optical" phase signal are generated for adaptive feedback loops, driven by evolutionary optimization techniques. The pulse is then iteratively manipulated until the desired result is reached. Fig. 4-8 indicates the mains steps of a spatio-temporal adaptive procedure.

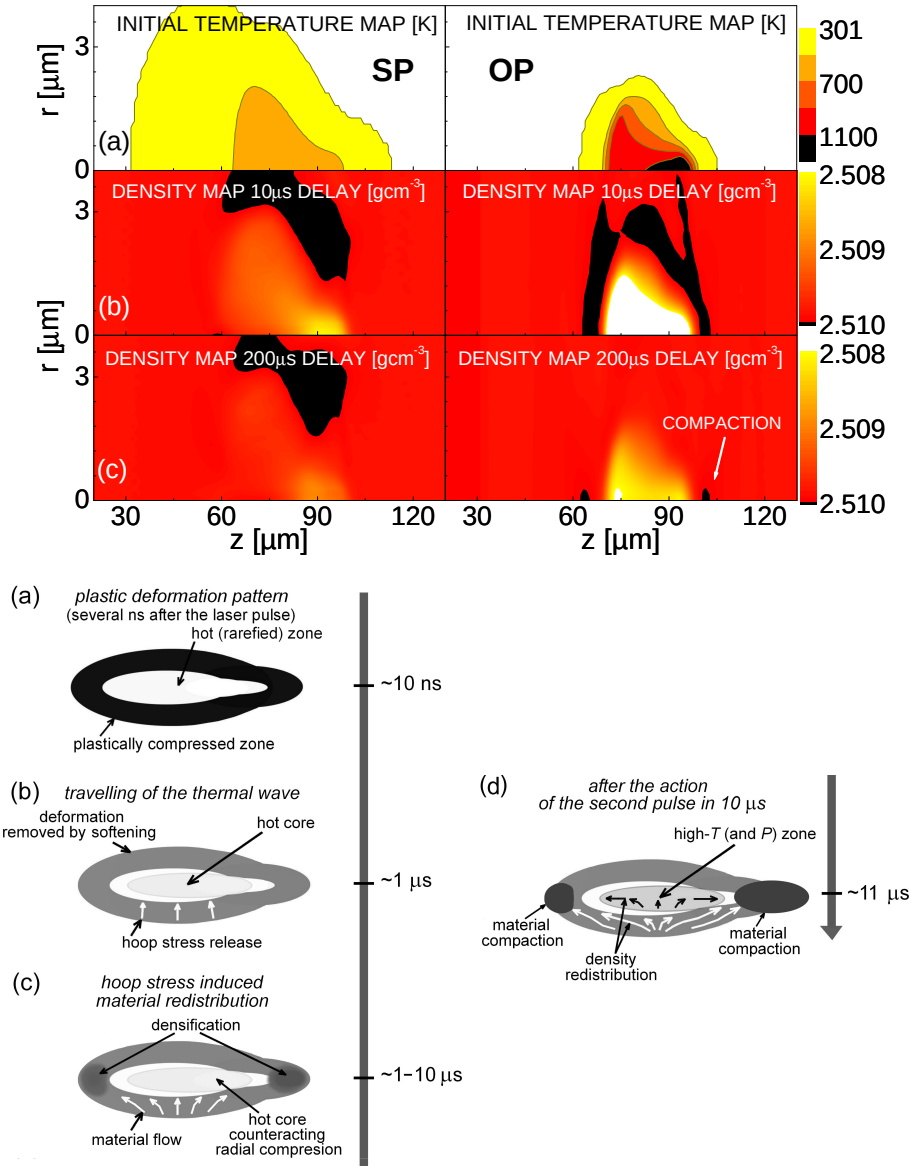

Fig. 4-10: Top: Excitation maps (absorbed energy) and subsequent material density maps in BK7 (thermo-elasto-plastic calculations) under standard (SP) and optimized (OP) single pulse excitation at 0.5 µJ. Axial compaction becomes visible for optimal pulse shapes. Bottom: Qualitative description of thermo-mechanical processes induced by picosecond laser irradiation. The picture emphasizes matter redistribution stages for single pulse irradiation: (a) the formation of the plastic layer as a result of the elasto-plastic wave, (b) softening of the plastic region upon heating, and (c) stress release and density redistribution. (d) The potential effect of a subsequent pulse arriving on approximately 10 µs is represented as well, showing the accumulation of compaction at high rates.

Optimization results: Usually, in glassy materials characterized by high expansion coefficients, ultrafast laser irradiation induces negative refractive index changes due to volume expansion and subsequent rarefaction. We have explored therefore the potential of regulated energy feedthrough in triggering laser-induced plasticity which results in establishing desired refractive index distributions. The experiments were performed in a material with a dominant "thermal" character, and, as a representative, we have chosen borosilicate crown BK7, a model glass with slow electronic relaxation, high expansion coefficients, and low softening point. This particular glass usually shows a decrease of the refractive index under standard ultrafast laser excitation. This behavior is associated with the formation of a hot region, where, due to rapid thermal expansion, the material is quenched in a low-density phase, rich in oxygen centers [EKT04, BSZ05]. Using laser radiation tailored on ps scales, a refractive index flip towards positive variations was observed in BK7, behavior depicted in Fig. 4-9 [MBS08-4]. This indicates the possibility to create waveguide structures (and symmetric guiding conditions) in materials that do not easily allow it in standard ultrafast irradiation conditions.

The mechanism was associated with the formation of a conical heat source and the behavior of the subsequent compression wave that drives axial compaction. Under ps irradiation, a transition from a radial expansion regime to a one-dimensional material flow is observed. The ps sequence allows higher energy concentration and the achievement of a elevated temperature due to a less efficient plasma generation and light defocusing. Narrow spatial distributions determine plastic deformation accompanied by partial healing of the lateral stress due to preferential heat flow. The matter momentum relaxation leads to axial densification and to a positive refractive index change. The adaptive technique was able to determine an excitation sequence which induces a thermo-mechanical path leading to compaction. This is particularly interesting for laser repetition rates, on the timescale of mechanical relaxation (hundreds of kHz) and shows the importance of the heating and relaxation rates. Similar behaviors were noted on phosphate and heavy-metal-oxide glasses.

Simulation tools: The above experiments were accompanied by comprehensive theoretical analyses involving optical energy deposition, thermodynamical evolution, and mechanical relaxation in order to identify, activate, and understand laser-induced mechanisms for material compaction. The numerical code developed to describe and analyze the nonlinear pulse propagation in transparent materials was used to determine excitation footprints in BK7. We recall that the model involves key features of nonlinear propagation and excitation (Kerr self-focusing, plasma generation and defocusing, phase modulation). The maps of absorbed

energy density were subsequently connected to a thermo-elasto-plastic formalism to quantify laser-induced material deformation and densification (Fig. 4-10). We have demonstrated that the hydrodynamic flow of softened material can move away from radial thermal expansion and be guided to form a visible region of compressed matter. An example is given which indicates the onset of axial densification in BK7 under optimal excitation conditions. Simulations approaches were developed in collaboration with the Institute of Thermophysics (N. Bulgakova) and Institute of Hydrodynamics (Y. Meschcheryakov) Novosibirsk and were also the object of a postdoc stay of I. Burakov at LabHC.

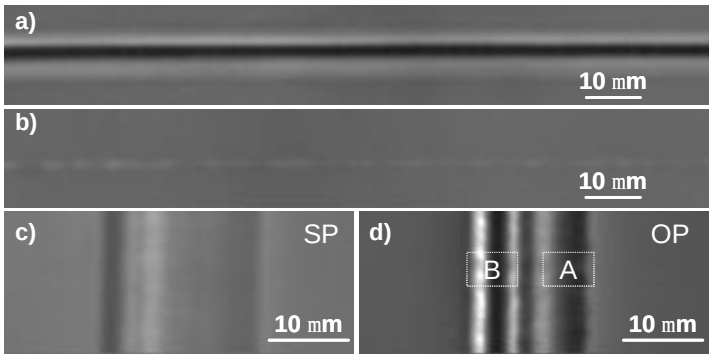

Fig. 4-11: (a) Short pulse longitudinal waveguides at high repetition rates (100 kHz) in BK7. The energy per pulse was 1.1 µJ and the scan velocity was 50 µm/s. A high positive index contrast is observed. (b) Trace made by longitudinal scan using 0.25 µJ short pulses. The index change is dominantly negative. (c) Transverse trace written by short laser pulses in the conditions of (a) at a scan velocity of 50 µm/s. (d) Transverse trace written by optimal laser pulses in the conditions of (a) at a scan velocity of 50 µm/s. Two regions of positive refractive index changes are indicated by the labels A and B.

It should be nevertheless observed that the thermomechanical model indicate a tendency of axial stress accumulation, without fully explaining the scale and the magnitude of the modification. The photochemical changes of the glass matrix including impurity transport and bond-breaking and reorganization upon multipulse exposure concur nevertheless to the final laser-induced modification.

e) regime of compaction: By coupling the experimental and simulation approaches, a compaction regime was determined for borosilicate crown glasses (BK7) at moderate laser repetition rates (100 kHz). This leads to positive refractive index changes when relatively high energy density is preserved (Fig. 4-11). Parts a) and b) show positive, respectively, negative index changes as a function of laser energy. The conclusions may be extended to other glasses characterized by high expansion coefficients. Experiments are in progress together with the Institute of Optics Madrid for the inscription of functional optical structures in bulk samples of heavy-metal oxide glasses and Er-doped laser glasses [SFA05, FDS07].

f) size correction via nonlinearity control. Nonlinearity control using elongated pulse forms indicates the possibility of regulating the structuring precision in the presence of

wavefront distortions [MRS08-1]. When wavefront aberration occur, the length of the laser-induced structure augments, which is detrimental to the photoinscription precision. The focal elongation influences the nonlinear energy deposition and modulation of the refractive index appears in the exposed region. If usually spatial corrections are applied to correct wavefront distortions, we have indicated that the energy can be as well confined using judicious temporal pulse shapes. Via a competition between self-focusing and ionization, adaptive control of nonlinearity can regulate the filamentary propagation and the characteristics of the optical damage [HSL06, ASW06, SGH06, LHZ05]. These observations showed flexibility in manipulating propagation, ionization, and energy gain events generated by ultrashort laser pulses in nonlinear environments using judicious intensity adjustments.

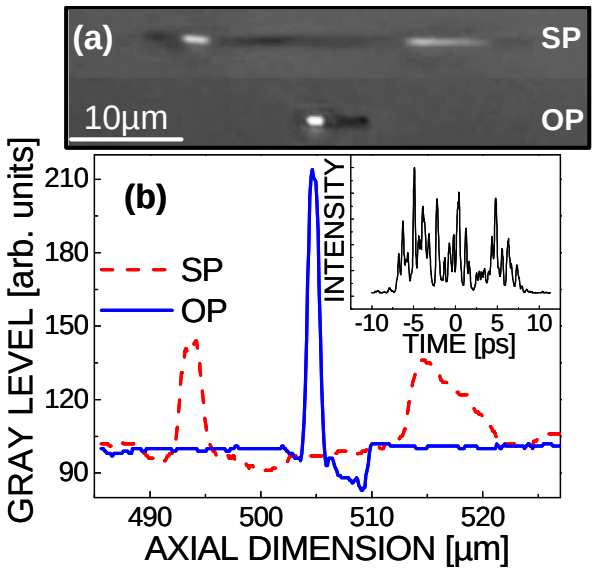

Fig. 4-12: (a) Short pulse (SP) and optimal pulse (OP) induced structures in a-SiO_2 at a depth of 500 μm and 1 µJ input energy indicating the spatial confinement of the OP structure in the presence of aberrations. (b) The corresponding axial cross-sections. The inset shows the optimal pulse shape.

Fig. 4-12 shows a situation were standard irradiation focused at significant depths in the presence of aberrations determines an elongated trace, together with the corrected trace. The adaptive temporal shaping induces spatio-temporal pulse behaviors able to localize energy on limited spatial scales, determining as well a dominant region of refractive index increase. A simplification of the control landscape allowed us to conclude that the main mechanism is related to two factors: negative shift generated by the plasma onset and an augmentation of the modification threshold at longer pulse durations. The decreased nonlinearity and the lower ionization efficiency assist the energy confinement while reducing the structure ellipticity and offer potential benefits for 3D optical processing. Recently, control of photoionization using asymmetric intensity envelopes at surfaces has shown a surprising reduction of the damaged area well below the diffraction limit [ERB07].

4.3 Adaptive optimization of refractive index changes in the spatial domain

a) Adaptive wavefront corrections: In many cases, laser 3D processing of bulk materials involves light passage through dielectric interfaces. Focusing through air-dielectric interfaces creates wavefront distortions due to refraction into different cone angles at the interface, as illustrated in Fig. 4-13. The figure indicates various points of energy concentration and the corresponding energy spread.

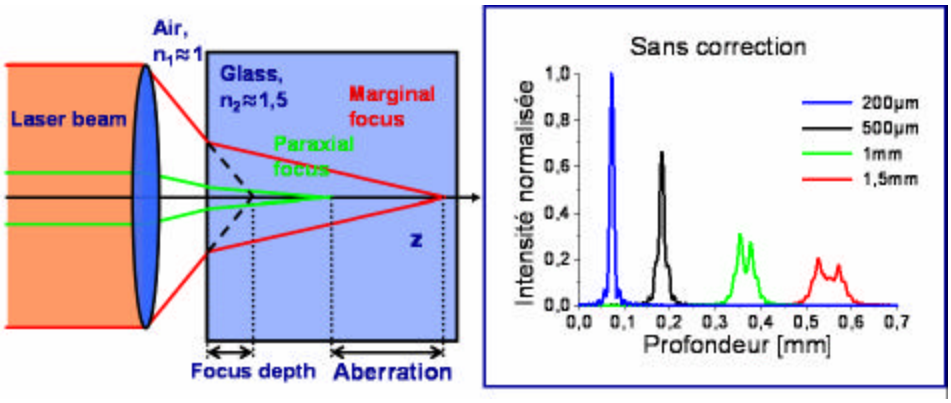

Fig. 4-13: Graphical description of spherical aberration due to refraction at air-dielectric interfaces with subsequent elongation of the focal area and calculus of axial intensity distribution for a focusing objective with a numerical aperture NA of 0.45.

The effects of spherical aberration in material processing were previously analyzed via several techniques including depth-dependent modification thresholds and aspect ratio measurements [MMM03, SJYG05]. Corrective functions using optical focusing designs or adaptive optics were employed to preserve the intrinsic energy confinement [HTC05, BSM06].

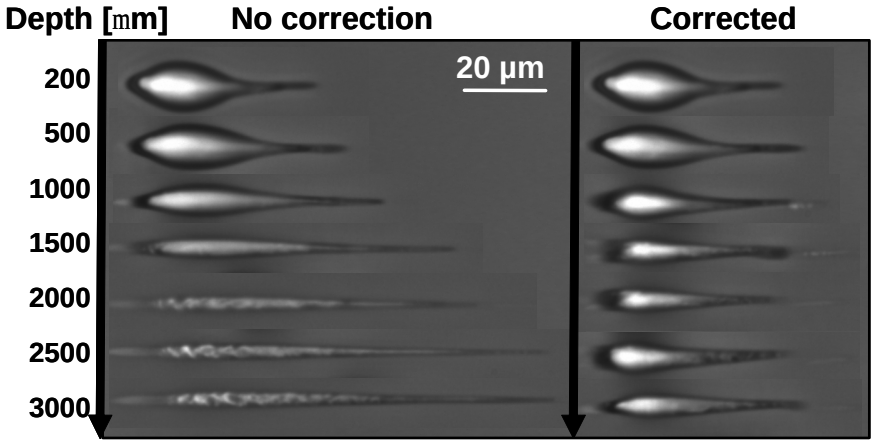

Fig. 4-14: Non-corrected (left) and spatially-corrected (right) laser irradiation results in BK7 showing laser energy confinement at different focusing depths.

Generally, when significant depths are required, these wavefront aberrations alter dramatically the energy confinement during propagation and on the morphology and homogeneity of laser-induced structures. This is particularly important for laser writing of

longitudinal waveguides, where the quality of photoinscription degrades with the focusing depth. The consequences are manifold; increased losses, inhomogeneous modulation of index contrast, or the apparition domains.

Using a comprehensive analysis of spherical aberration, we have calculated the wavefront distortions upon focusing using a scalar diffraction theory [HSA07-5]. An undesirable elongation of the focal area was shown which limits the energy deposition efficiency. Solving the propagation equations through the dielectric interface, corrective solutions were proposed to preserve a high resolution.

In parallel, with emphasis on applications in waveguiding technologies, we have established an adaptive method for dynamic correction of wavefront aberrations and synchronization with the laser photoinscription process. Using adaptive programmable spatial tailoring of the ultrafast laser beam integrated in a control loop, we showed that the spherical aberration can be dynamically compensated during the writing process. The approach is based on spatial phase retardation introduced by programmable optical modulators responding to a feedback derived from the laser action and being driven by a global optimization strategy (Fig. 4-8) [HKL06]. Using microscopy-based loops, aberration-free structures can be induced at arbitrary depths, showing higher flexibility for 3D processing. Examples are given in Fig. 4-14, describing the efficiency of energy localization when spatial corrective procedures are utilized [CAS08-3].

The employment of dynamic procedures for wavefront aberration enables transporting the laser energy to the impact point without significant spatial dispersion. Besides delivering constant excitation conditions and upgraded uniformity, it is possible to preserve sufficient concentration of energy in special glasses to trigger mechanisms of thermo-mechanical compaction as it was demonstrated in the BK7 case [CAS08-3]. To obtain a full benefit, attempts to introduce spatial phase information in the nonlinear propagation codes are under way. Possibilities to control and correct beam delivery setups are envisaged.

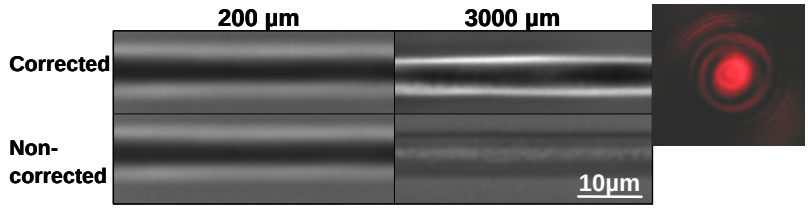

Fig. 4-15: Waveguide writing in BK7 under corrected irradiation conditions. Guiding is observed on significantly longer distances when wavefront corrective procedures are utilized.

b) Dielectric processing: Using spatio-temporal pulse design and adaptive correction techniques, quality waveguides with high index contrast were generated over significant

regions under tight focusing conditions (Fig. 4-15). This represents a welcomed extension of the longitudinal writing conditions for symmetric waveguiding, with potential in delivering homogeneous and low loss waveguides.

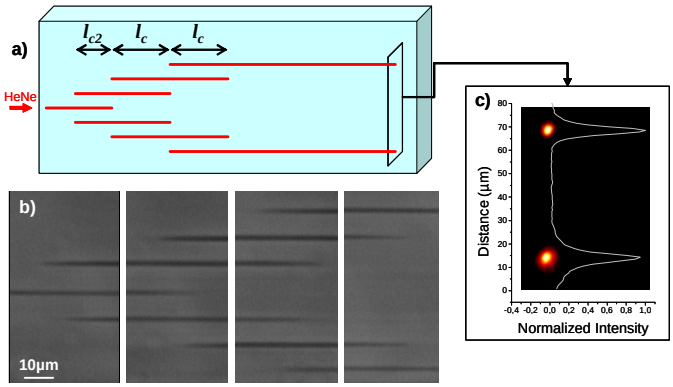

Fig. 4-16: 2D beam-splitting function in evanescently-coupled waveguide arrays in a –SiO_2.

Current efforts are made for parallel writing of complex trace matrices to study collective propagation phenomena in evanescently coupled waveguide arrays. An example showing 2D and 3D beam splitting functions is depicted in Fig. 4-16. Furthermore 2D, 3D couplers and WDM dividers were demonstrated.

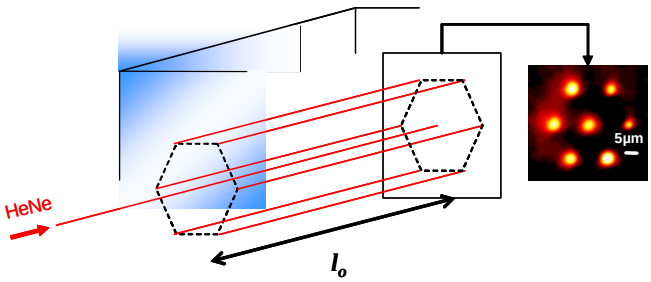

Fig. 4-16:3D beam-splitting function in evanescently-coupled waveguide arrays in a–SiO_2.

4.4 Summary

If energy deposition is a delicate balance between absorption, losses, and thermodynamic evolution, temporal tailoring of laser pulses can be very effective in controlling this balance, changing the energy coupling, and, in such, determining the overall development of the irradiated system. Modulated light can act on different timescales, either corresponding to electronic excitation and exploiting fast changes of the dielectric function, or taking advantage of thermally-induced structural phase transition where the relevant parameter becomes the timescale of electron-vibration coupling and lattice deformations. Prerequisites for better absorbing and transforming the laser energy are created, using light modulation techniques integrated in adaptive feedback loops. The measured output is fed back into an iterative loop until an excitation sequence is derived which achieves an optimal

experimental signal. Global optimization strategies may thus be applied, even if no information on the physical process is initially at hand, while the optimal result can provide extended information on the control mechanisms.

The pulse temporal form is therefore an efficient factor to store energy in the material, to generate and accelerate ions, to form tailored nanoparticles, or to regulate the structural transition, density variations, and stress repartition generated upon bulk transformation. Suitable pulse shapes enables the exploit of optical transients and induce an improvement of the energetic coupling. Particularly for complicated interactions, adaptive optimization may deliver the most effective way to drive the system in pre-specified states. Efficient ablation with low residual stress can be obtained, as well as particular surface properties by triggering polymorphic transformations or designed changes of the dielectric function. Control of refractive index changes may be enabled by mastering laser-induced thermo-mechanical effects on the timescale of mechanical relaxation. We have shown that the standard response of materials can be tailored, indicating how plasticity can be used for materials with high volume expansion by enforcing key control factors; size, geometry, and the temperature level of the heat source. Additionally, dynamic control of the spatial phase is an effective way to fulfill corrective functions, compensating for eventual wavefront distortions, creating arbitrary excitation designs, or offering possibilities for nonlinearity control. However, despite the "blind" nature of the adaptive approach, designing the resulting modification for practical applications can only be based on extensive knowledge of the nature of light-matter interaction, which, in turn, will lead to viable concepts for optimizing laser interactions. Adaptive schemes in spatio-temporal domains can thus have an extended range of action, enabling applications that could largely benefit from light-matter synergies.

List of selected papers for presentation:

1) A. Mermillod-Blondin, A. Rosenfeld, J. Bonse, I. V. Hertel, C. Mauclair, E. Audouard, and R. Stoian "Size correction in ultrafast laser processing of fused silica by temporal pulse shaping" Appl. Phys. Lett. 93, 021921 (2008)

2) J. P. Colombier, P. Combis, E. Audouard, and R. Stoian "Transient optical response of ultrafast non-equilibrium excited metals: Evidence of an electron-electron contribution to collisional absorption" Phys. Rev. E 77 036409 (2008)

3) C. Mauclair, A. Mermillod-Blondin, N. Huot, E. Audouard, and R. Stoian "Dynamic correction of wavefront distortions during ultrafast laser writing of longitudinal waveguides in optical glasses" Opt. Express 16, 5841 (2008)

4) A. Mermillod-Blondin, I. M. Burakov, Yu. P. Meshcheryakov, N. M. Bulgakova, E. Audouard, A. Rosenfeld, A. Husakou, I. V. Hertel, and R. Stoian “Flipping refractive index changes in ultrafast laser-irradiated optical glasses” Phys. Rev. B 77, 104205 (2008)

5) N. Huot, R. Stoian, A. Mermillod-Blondin, C. Mauclair, and E. Audouard “Analysis of the effects of spherical aberration during ultrafast laser-induced refractive index variation in optical glasses” Opt. Express 15, 12395 (2007)

6) J.P. Colombier, P. Combis, A. Rosenfeld, I.V. Hertel, E. Audouard, and R. Stoian “Optimized energy coupling at ultrafast laser irradiated metal surfaces by tailoring intensity envelopes. Consequences for material removal from Al samples” Phys. Rev. B 74, 224106 (2006)

7) R. Stoian, A. Mermillod-Blondin, A. Rosenfeld, I.V. Hertel, M. Spyridaki, E. Koudoumas, P. Tzanetakis, C. Fotakis, and N.M. Bulgakova “Optimization of ultrafast laser generated low-energy ion beams from silicon targets” Appl. Phys. Lett. 87, 124105 (2005)

8) R. Stoian, A. Mermillod-Blondin, S. W. Winkler, A. Rosenfeld, I.V. Hertel, M. Spyridaki, E. Koudoumas, P. Tzanetakis, C. Fotakis, I.M. Burakov, and N.M. Bulgakova “Temporal pulse manipulation and consequences for ultrafast laser processing of materials” Opt. Eng. 44, 051106 (2005)

Conclusions

The present research activity has indicated that control of laser-induced effects in processing materials is possible and the energy coupling can be optimized, as well as the material response to ultrafast excitation, relying on the exciting pulse rather then on the engineered photosensitivity of materials. The outcome is an improved laser structuring approach with additional flexibility, accuracy, and a higher degree of process control. This has relevance for upgrading current laser processing technologies, provides improved solutions to current limitations, and offers a better understanding of the laser-induced physical processes. The control factors were identified in the absorption phase, in the degree of non-equilibrium, as well as in the succession of phase transitions.

The research development followed an axis defined by the study of laser ablation mechanisms and their time evolution at surfaces and in the bulk, and focused on identifying the factors of control and improvement of the structuring process. After a brief discussion of excitation mechanisms, non-thermal and thermal processes were indicated, among them the impulsive electrostatic disruption of the surface (Coulomb explosion) and the delayed, thermally induced ablation, together with the appearance of various ablation phases. The nature of the ablation products was studied from a kinetic perspective. Modeling approaches were developed to account for the energy transport and to quantify the disruptive charging field or the thermal load of the materials. Hydrodynamic models were used to analyze the dynamics of phase transformation in conditions of initial non-equilibrium. Nonlinear pulse propagation was followed inside transparent materials and the resulting absorption and material response in terms of density changes were calculated. The potential of viable techniques for refractive index engineering and optical functionalization was evocated.

Based on the information gained from time-resolved observations of the succession of transformation phases, the possibility to influence the material sequence of thermodynamic phase transformations and to balance the energy coupling efficiency was indicated and various options for control and optimization were discussed. The concept of optimizing laser interactions, based on the possibility to regulate energy delivery, has stimulated new paths of research in material processing. Using temporal pulse forming, control may be achieved on the chemical composition and the kinetic properties of the ablation products, as well as on the structural changes of the irradiated material. The potential spectrum of applications ranges from quality structuring for increased functionality to integration in analytical methods,

sensitive to particle emission, but designing material removal characteristics can be appealing for a broader range of applications. Experimental and theoretical results were consequently discussed, showing the possibility to attain desired structural modifications in bulk transparent materials. Examples were given concerning refractive index changes in glasses which are otherwise difficult to process. We recall that positive refractive index variations are mandatory for waveguiding in bulk materials in view of possible optical integration. Insights into the dynamics of energy relaxation were obtained, delivering the guidelines for the relevant timescales in pulse tailoring. Corrective procedures based on spatial pulse shaping were tested to enhance the accuracy and the potential of 3D processing.

These results indicate as well important consequence for material processing, responding thus to the present challenges in the field. New directions of development were shown to advance matter and shape adaptable technologies. Potential for increasing the efficiency and the quality of the structuring process was indicated while guiding the material response. Novel properties and functions are attached in this way to the material, laying a groundwork for adaptive optimization in material processing. At the same time the new techniques offer additional physical insight into the mechanisms of control. More knowledge about the nature of interaction becomes available. This fosters advance into understanding the nature of material modification, including the ability to identify competitive relaxation processes. The present organizational structure has equally enabled a platform of industrial insertion. The possibility of technological transfer via the laser structuring platform of the Pole Optique Rhône-Alpes is envisaged. By exploiting the enhanced flexibility of femtosecond technology for 3D processing, we believe that benefits are foreseeable in several application sectors such as information and telecommunication technologies, security, medical applications, sensorics, etc.

Perspectives

The synthesis of results and ideas presented so far facilitated a reflection moment concerning the future of these technologies, and, within, the prospects of my own activity. The perspectives of the activity I have described in this work follow the general effort in generating reliable, rapid, and flexible processing tools which are moreover matter and shape-adaptable. They can be grouped in two main categories with potential in both applications and fundamental studies, with the purpose to cross the gap between potential and real opportunities for technological implementation.

Our present activity for understanding and controlling ablation or laser modification will be extended, especially in that concerns the effects of energy relaxation times scales and their prospect in using relevant tailored radiation in glasses and crystals. A specific interest is put into the optical damage mechanisms in high-n dielectrics used in dielectric gratings for high power laser applications. This requires an update of the time-resolved imaging techniques, including the potential of quantitative phase microscopy and time-resolved birefringence measurements in order to determine light-induced anisotropies. A second phase involving time- and space-resolved spectroscopic investigations on laser-induced structures is planned in cooperation with the "spectroscopy" team of the LabHC (A. Boukenter). The emphasis will be put in the formation of optically active defects which may additionally contribute to refractive index changes as well as the interrogation of the vibration activity during relaxation and the onset of densification. A material survey is planned to detect relevant macroscopic material characteristics. A PhD thesis focused on this theme has recently started (K. Mishchik).

The activity in the field of processing of transparent materials will go on with attempts to optical functionalize (adding waveguiding functions) Raman active glasses or tungstate-based materials for broad band generation, as well as more classical optical glasses. This will follow two paths, refractive index engineering and parallel processing of embedded structures. The point-spread-function engineering together with parallel writing methods indicate a significant potential for rapid prototyping and fast inscription of complex structures. Additionally we will continue our research concerning structural transitions in conditions of energy and stress confinement. The detection methods based on phase and birefringence observation will be updated towards quantitative measurements. A special emphasis will be put in formation of waveguide arrays and evanescent mode coupling, showing resonant

collective effects. The research activity has already started in the frame of the postdoc stay of G. Cheng.

As a follow-up of our activity in developing simulation tools for laser ablation, we plan to further extend the nonlinear propagation codes in the presence of wavefront distortions, non-paraxiality, as well as propagation of exotic pulse profiles. The numerical activity can show how far the nonlinearity can be controlled by spatio-temporal design with respect to excitation and propagation. Concerning the non-transparent materials and interfaces, we intend to insert numerical adaptive loops into the hydrodynamic code for simulating user-designed thermodynamic states and predicting associated properties. The hydrodynamic code will be further developed to consider the effect of specific density of states on transport material properties. A radiative transfer module will be added. The pulse shaping activity will be extended to other laboratory projects involving plume control for PLD application and nanoparticle generation.

As the scale of modification zone becomes smaller and smaller, nanoscale and plasmon-coupled near field phenomena grow to be increasingly significant. An important subject to be investigated concerns the possibility to perform nanostructuring, either at single point using wavefront corrections or parallel (multi-focus) nano-machining using spatial beam shaping, multibeam interferences and Talbot effect. For complex patterns, periodic or non-periodic, adaptive wavefront shaping will be involved. Additionally, polarization control in spatial and temporal domains can be used as an effective factor in determining the matter response on nanoscale, as well as the post-process coupling of light in nanostructured materials. Applications in laser marking or information storage are foreseen. This work will be performed in by the LabHC “Ultrafast processing group” and the “Laser processing platform” under the frame of two ANR projects (ANR Chair d’Excellence AdPRO 2005-2008 and ANR Nanomorphing 2007-2010).

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